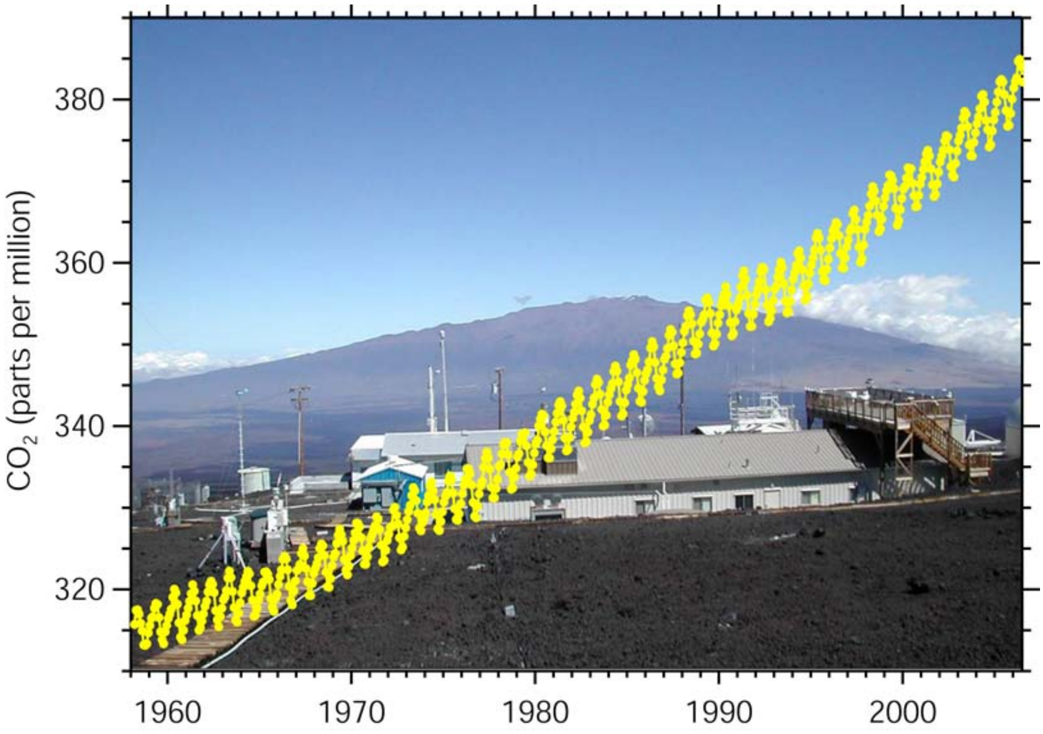
WORLD METEOROLOGICAL ORGANIZATION
GLOBAL ATMOSPHERE WATCH

13TH WMO/IAEA Meeting of Experts on Carbon Dioxide Concentration and Related Tracers Measurement Techniques

(Boulder, Colorado, USA, 19-22 September 2005)

No. 168



December 2006

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The cover graphic shows the U.S. National Oceanographic and
Atmospheric Administration Mauna Loa atmospheric observatory
and the nearly fifty year monthly-mean CO_2 signal
measured there from 1958 to 2006.
The data used to construct the monthly means are
from Scripps Institution of Oceanography
(1958 to 1974) and NOAA (1974 to present).

Edited by John B. Miller

World
Meteorological
Organization
Weather • Climate • Water

WMO TD No. 1359

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DEDICATION

Charles David (Dave) Keeling 1928 – 2005

(Source: Scripps Institution of Oceanography: Contact Scripps Communications: (858) 534-3624 or scrippsnews@ucsd.edu)

Dave Keeling's scientific career began with a post doctoral position at Caltech in 1953. There he commenced a study aimed at extracting uranium from granite rock with applications in the nuclear power industry. However, this work soon gave way to another project involving the equilibria between carbonate in surface waters, limestone and atmospheric CO_2. He found significant variations in the concentration of atmospheric CO_2 near Pasadena, probably due to industry, and moved his sampling equipment to Big Sur near Monterey.

Here he began to take air samples throughout the day and into the night and soon established an intriguing diurnal pattern. The air contained more CO_2 at night than during the day and, after corrections for water vapour were made, had about the same amount of CO_2 every afternoon, 310 parts per million (ppm). He used stable isotope ratio mass spectrometry measurements of the CO_2 he extracted to show that the $^{13}C/^{12}C$ ratio in CO_2 at night was smaller than during the day and a function of plant respiration. These measurements were repeated in other remote locations and everywhere the data were the same: strong diurnal behaviour with steady values of about 310 ppm in the afternoon.

The explanation for these puzzling results came from a book on meteorology describing diurnal patterns in turbulence in the atmosphere. In the afternoon Dave Keeling was measuring CO_2 concentrations representative of the "free atmosphere", concentrations that prevailed over a large part of the Northern Hemisphere. Little did he know then that he had laid the basis for his remarkable career spanning almost 5 decades documenting the global behaviour of atmospheric CO_2.

In 1958 he installed one of four non-dispersive infrared gas analysers at a remote site at 3400m above sea level on Mauna Loa, a volcano in Hawaii. In March of that year he measured a background atmospheric CO_2 concentration of 313 ppm. However, to his surprise the CO_2 concentration had risen 1ppm by April 1958 to a maximum in May when it began to decline reaching a minimum in October. After this the concentration increased again repeating the same seasonal pattern in 1959. In Dave Keeling's words "We were witnessing for the first time nature's withdrawing CO_2 from the air for plant growth during summer and returning it each succeeding winter". Dave Keeling's analytical skills and dedication had paid off with two dramatic discoveries. First, the seasonal "breathing" of the planet and second, the rise in atmospheric CO_2 due to the combustion of fossil fuels by industry and emissions from land use changes, for example large scale burning of tropical forests. These remarkable findings marked the beginning of the world famous "Keeling Curve" now extending for almost five decades and representing one of the Earth's most important long term scientific records.

Dave Keeling's analytical methods were rigorous and traceable and leave us in the atmospheric community with a remarkable legacy. The "Keeling Curve" is without doubt the most important long term geophysical measurement ever made. But a simple glance at the curve carries a warning: the inescapable fact that at the start of the record 50 years ago long term growth rates of atmospheric CO_2 were under 1 ppm per year whereas now they are approaching 2 ppm per year. What heed will we as a species take of that warning?

Dave Lowe
Wellington, New Zealand

Note: Dave Keeling's autobiography "Rewards and penalties of monitoring the Earth" provides a candid and fascinating insight into the highs and lows of his remarkable career and is on line at: http://arjournals.annualreviews.org/doi/abs/10.1146/annurev.energy.23.1.25

GROUP PICTURE

ACRONYMS AND ABBREVIATIONS USED IN THIS REPORT

I. Institutional

CarboEurope IP	CarboEurope Integrated Project, an EU project on European carbon balance
CCGG	Carbon Cycle Greenhouse Gases group of the NOAA/ESRL
CCL	Central Calibration Laboratory
CDIAC	Carbon Dioxide Information Analysis Centre (USA)
CEA-CNRS	Commissariat a l'Energie Atomique - Centre National de la Recherche Scientifique (French Nuclear Energy Agency – National Centre for Scientific Research)
CMA	China Meteorological Administration
CMDL	Climate Monitoring and Diagnostics Laboratory (U.S.A.)
CSIRO	Commonwealth Scientific and Industrial Research Organization (Australia)
CU	University of Colorado, Boulder
ECMWF	European Centre for Medium-range Weather Forecasting
ENEA	Ente per le Nuove Tecnologie, L'Energia e L'Ambiente (Italian National Agency for New Technology, Energy and the Environment)
ESRL	Earth System Research Laboratory (the former Climate Monitoring and Diagnostics Laboratory – CMDL -- is now part of this laboratory)
GAW	Global Atmosphere Watch (a WMO programme)
GCP	Global Carbon Project
Globalview	A cooperative atmospheric data integration project
GMD	Global Monitoring Division of the NOAA/ESRL
GOOS	Global Ocean Observing System
GTOS	Global Terrestrial Observing System
IAEA	International Atomic Energy Agency
IGACO	Integrated Global Atmospheric Chemistry Observation (system), a WMO programme
IGBP	International Geosphere-Biosphere Programme
IGCO	Integrated Global Carbon Observation
IHDP	International Human Dimensions Programme
INSTAAR	Institute for Arctic and Alpine Research, University of Colorado
ISO	International Organization for Standardization
IUPAC	International Union of Pure and Applied Chemistry
JMA	Japan Meteorological Agency
KMA	Korean Meteorological Administration
KRISS	Korea Research Institute of Standards and Science
LSCE	Laboratoire des Sciences du Climat et de l'Environnement (Laboratory for Climate and Environmental Science) (France)
MPI-BGC	Max-Planck Institut für Biogeochemie, Jena, Germany
MSC	Meteorological Service of Canada
NACP	North American Carbon Programme
NCAR C-DAS	National Centre for Atmospheric Research Carbon Data-Model Assimilation System
NIAIST	National Institute of Advanced Industrial Science and Technology (formerly National Institute for Resources and Environment -- NIRE) (Japan)
NIES	National Institute for Environmental Studies (Japan)

NIST	National Institute of Standards and Technology
NIWA	National Institute of Water and Atmospheric Research (New Zealand)
NOAA	National Oceanic and Atmospheric Administration (U.S.A)
OSSE	Observing System Simulation Experiment
PI	Principal Investigator
QA/SAC	Quality Assurance/Science Activity Centres (part of WMO/GAW)
RAMCES	LSCE atmospheric greenhouse gas network
SAG	Scientific Advisory Group
SIO	Scripps Institution of Oceanography
SOPs	standard operating procedures
TACOS	Terrestrial and Atmospheric Carbon Observing System (an EU programme)
TCO	Terrestrial Carbon Observations
UEA	University of East Anglia
UNFCCC	United Nations Framework Convention on Climate Change
WCC	World Calibration Centre
WCC-Empa	WCC - Eidgenossische MaterialPrufungsAnstalt (Switzerland)
WCRP	World Climate Research Programme
WDCGG	World Data Centre for Greenhouse Gases (a WMO programme)
WMO - AREP	WMO Atmospheric Research and Environment Programme

II. Technical/Scientific

AVD	Absolute Volumetric Determination
cat/GC-FID	CO analysis technique with catalytic reduction of CO to CH_4, followed GC-FID
CARIBIC	Civil Aircraft for Regular Investigation of the atmosphere Based on an Instrument Container
CARIBOU	An automated NDIR CO_2 analyzer used by LSCE
CLASSIC	Circulation of Laboratory Air Standards for Stable Isotope inter-Comparisons
DBMS	Data Base Management System
ECD	Electron Capture Detector. Typically used in conjunction with gas chromatography.
FID	Flame Ionization Detector. Typically used in conjunction with gas chromatography.
GG	Greenhouse Gases
HITRAN–04	HIgh-resolution TRANsmission molecular absorption database - 2004 version
ICP	Inter-comparison Project
IHALICE	International HALocarbon in Air Comparison Experiment
LOFLO	A low volume NDIR CO_2 analyzer
LN_2	Liquid Nitrogen (coolant)
MOPITT-TERRA	Measurements Of Pollution In The Troposphere (NASA satellite-borne sensor for CO)
MOZAIC	Measurement of ozone, water vapour, carbon monoxide and nitrogen oxides aboard Airbus in-service aircraft
NBS 19 and 20	National Bureau of Standards calcite standards for isotopic ratio measurement (NBS is now National Institute for Standards and Technology – NIST)
NDIR	Non-Dispersive InfraRed (CO_2 analyzer)

OCO	Orbiting Carbon Observatory (planned NASA satellite-borne CO_2 sensor)
PAN	PeroxyAcetylNitrate
per mil (per meg)	part per thousand (million) deviation from a reference value, ~~respectively~~. Per mil is used in reporting stable isotope (e.g. $\delta^{13}C$) and per meg for O_2/N_2 results. Typically used with δ-notation: $\delta = \left(\frac{R_{sample}}{R_{reference}} - 1 \right) 10^3$ per mil (or 10^6 for per meg)
ppm (ppb, or ppt)	parts per million (10^6) (billion -- 10^9, or trillion – 10^{12}). When used in reporting mixing ratios (mole fractions), defined as moles of trace gas per mole of dry air, where, e.g.: 1 ppm CO_2 = (10^{-6} mole CO_2)/(mole of dry air)
PTFE	polytetraflouroethylene
QA/QC	quality assurance/quality control
rms	root mean square (error)
RGD	Reduction Gas Detector
sccm	standard cubic centimeters per minute (volumetric flowrate normalized to ~~STP~~)
SCIAMACHY	SCanning Imaging Absorption SpectroMeter for Atmospheric CHartographY (ESA satellite-borne mutli-species sensor)
SRM	Standard Reference Material
TDLAS	Tunable Diode Laser Absorption Spectroscopy
VOCs	volatile organic compounds
VPDB	Vienna Pee Dee Belemnite (stable isotopic standard material)
VSMOW	Vienna Standard Mean Ocean Water (stable isotopic standard material)
VUV	Vacuum UltraViolet. Used with reference to a flouresence technique used to measure carbon monoxide.

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THE WMO GLOBAL ATMOSPHERE WATCH (GAW) PROGRAMME

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1. INTRODUCTION

The Global Atmosphere Watch (GAW) Programme of the World Meteorological Organization (WMO) was established in 1989. It is focused upon the role of atmospheric chemistry in global change (Strategic Plan, 2001; Strategic Plan Addendum, 2004). Consisting of a partnership of managers, scientists and technical expertise from 80 countries, GAW is coordinated by the WMO Secretariat in Geneva and the Working Group on Environmental Pollution and Atmospheric Chemistry (WG-EPAC) of the WMO Commission for Atmospheric Science (CAS). The international greenhouse gas measurement community that met at this 13th meeting co-sponsored by WMO and IAEA are involved in nationally funded measurement programmes that constitute the global long term greenhouse monitoring network supported by GAW. The first meeting of this group, held in 1975 at Scripps Institute of Oceanography, was co-sponsored by WMO (Figure 1). It was a milestone in leadership of global greenhouse gas monitoring by US-NOAA. Comparison of this small group with the large group (page v) in the photo of this meeting shows how much our community has grown. Note that two members are in both pictures: Dr David Lowe of New Zealand and Professor C.S. Wong of Canada.

Figure 1: The 1st WMO sponsored CO_2 experts meeting at Scripps, La Jolla, California, 1975. Back left to right: Dave Lowe (New Zealand), Ernie Hughes (NIST), Bob Bacastow (Scripps), Don Pack (1st dir. of NOAA/GMCC), Walter Bischof (Sweden), Arnold Bainbridge (Scripps), C.S. Wong (Canada), Ken Pettit (AES, Canada), Walter Komhyr (NOAA). Front left to right Graeme Pearman (CSIRO, Australia), Michel Benarie (IRCHA, France), Lester Machta (NOAA), Charles (Dave) Keeling(Scripps) and G. Kronebach of WMO Secretariat, Geneva (photo supplied courtesy of P. Tans).

The WMO/GAW office and leaders of its Scientific Advisory Groups (SAGs) have been actively involved in supporting the United Nations Framework Convention on Climate Change (UNFCCC) through contributions to the Strategic Implementation Plan of the Second Report on the Adequacy of the Global Observing Systems for Climate by the Global Climate Observing Strategy (GCOS). This plan is officially accepted by the Parties to the Convention. Essential Climate

Variables (ECVs) that need to be systematically measured globally in order to address major issues are officially recognized. Greenhouse gases, ozone and aerosols are amongst those ECVs and GAW is designated as the lead international programme in furthering the observational requirements. In October 2005, the steering committee of the Global Climate Observing System (GCOS) which is co-sponsored by WMO, approved the GCOS-GAW Agreement establishing the *"WMO-GAW Global Atmospheric* CO_2 *&* CH_4 *Monitoring Network*" as a comprehensive network of GCOS. The leadership of Dr James Butler in preparing the successful proposal is gratefully acknowledged. He was a member of the GCOS Atmospheric Observations Panel for Climate (AOPC) and represented the GAW Scientific Advisory Group for Greenhouse Gases (SAG-GG).

The focus, goals and structure of GAW are outlined in detail in the Strategic Implementation Plan 2001-2007 (GAW Report 142) and its addendum (GAW Report 156). Recognizing the need to bring scientific data and information to bear in the formulation of national and international policy, the GAW mission is threefold:

a. Systematic monitoring of atmospheric chemical composition and related physical parameters on a global to regional scale.
b. Analysis and Assessment in support of environmental conventions and future policy development.
c. Development of a predictive capability for future atmospheric states.

This mission is conducted through the ongoing activities of the group of experts representing carbon cycle research and measurements that were assembled at this 13th meeting and the GAW SAG-GG chaired by Dr Ed Dlugokencky that met after this expert meeting.

2. GAW MONITORING

GAW focuses on six measurement groups: greenhouse gases, UV radiation, ozone, aerosols, major reactive gases (CO, VOCs, NO_y and SO_2), and precipitation chemistry. The GAW Station Information System (GAWSIS) was developed and is maintained by the Swiss GAW programme. It is the host of all GAW metadata on observatory managers, location and measurement activities. According to GAWSIS there are 24 Global, 640 Regional and 73 Contributing stations are operating or have submitted data to a GAW World Data Centre. GAW Scientific Advisory Groups (SAGs) for each of the six measurement groups establish measurement standards and requirements while calibration and quality assurance facilities ensure valid observations. Five GAW World Data Centres collect, document and archive data and quality assurance information and make them freely available to the scientific community for analysis and assessments. Note the linkages of GAW to Contributing partner networks and to aircraft and satellite observations that contribute to Integrated Global Atmospheric Chemistry Observations (IGACO).

In the past decade, the emphasis of the GAW community on standardization, calibration, quality assurance, data archiving/analysis and building the air chemistry monitoring networks has resulted in major advances. Figure 2 shows the components diagram of the *"WMO-GAW Global Atmospheric* CO_2 *&* CH_4 *Monitoring Network*".

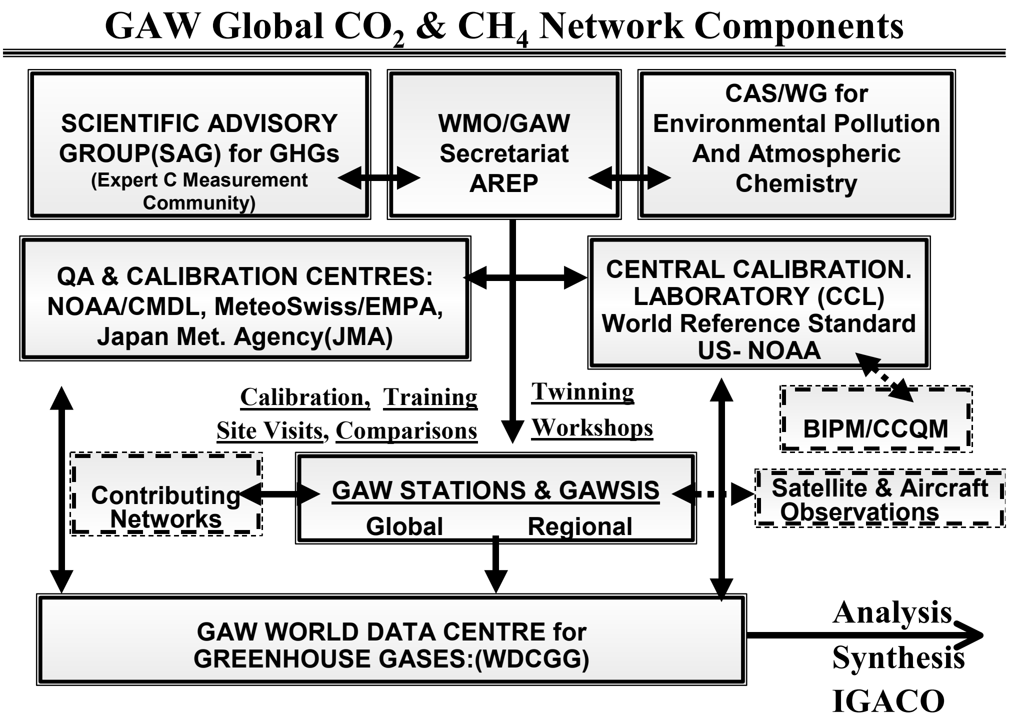

Figure 2: **Components of the WMO-GAW Global Atmospheric CO_2 & CH_4 Monitoring Network a comprehensive network of GCOS.**

There are GAW Global, Regional and Contributing stations that support the monitoring of GAW target variables in each of the six groups. Global and Regional stations are operated by a WMO Member and are defined by Technical Regulations adopted by the WMO Executive Council in 1992 (EC XLIV; 1992) as well as the GAW Strategic Implementation Plan (Strategic Plan, 2001; Strategic Plan Addendum, 2004). Contributing stations are those that conform to GAW measurement guidelines, quality assurance standards and submit data to GAW data centres. They are mostly in partner networks that fill major gaps in the global monitoring network. The difference between a Global and a Regional GAW station lies in the facilities available for long term measurements, the number of GAW target variables measured, the scientific activity at the site and the commitment of the host country. The location of the 24 GAW Global stations is shown in Figure 3a.

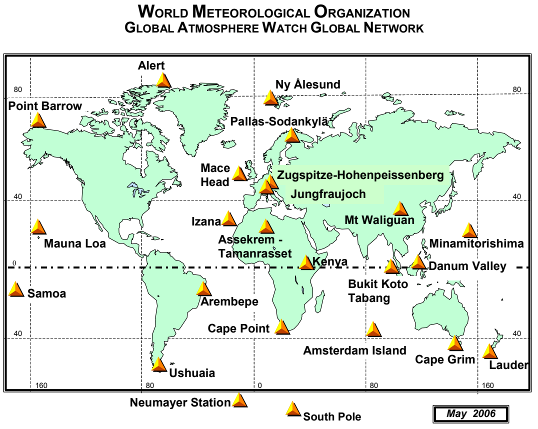

Fig. 3a
Global stations in the GAW network.

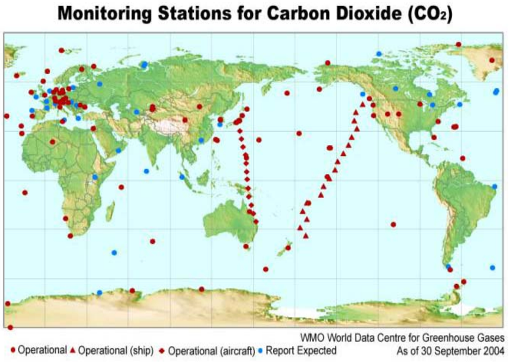

Fig. 3b
The GAW surface carbon dioxide network.

To monitor global distributions and trends of a particular variable with sufficient resolution to answer outstanding gaps in understanding of environmental issues related to global warming due to greenhouse gases requires not only Global but also Regional and Contributing stations. The GAW global network for surface based carbon dioxide observations is shown in Figure 3b. This differs from the global map of all stations at which carbon measurements and research are performed in that it represented stations operating routinely that link their observations to through the WMO reference scale maintained at NOAA GMD in Boulder and that submit their data to the GAW World Data Centre for Greenhouse Gases. In future, many more stations will hopefully be added to fill gaps in Asia, Africa and South America. Also, aircraft and satellite observations will be added as the integrated global atmospheric carbon observation system as outlined in the IGACO (2004) report is implemented through the WMO-GAW programme.

Where do carbon research and systematic observation programmes fit amongst the many projects, programmes, strategies and systems involved in global carbon observations? This is an often-asked question by many carbon cycle experts, managers and policy makers interested in the global carbon cycle and its impact on global change. One way of viewing the hierarchy of programmes and their connection to each other and to major users of the outcome of systematic observations research is shown in Figure 4. The hierarchy of activities starts with national efforts coordinated through GAW with linkage to the UNFCC through GCOS. In turn, it links to the satellite community through CEOS and the informal Integrated Global Observing Strategy (IGOS) that initiated development of the IGACO and IGCO strategies. The Global Earth Observation System of Systems also assists in linking to key societal benefit areas of global atmospheric carbon monitoring.

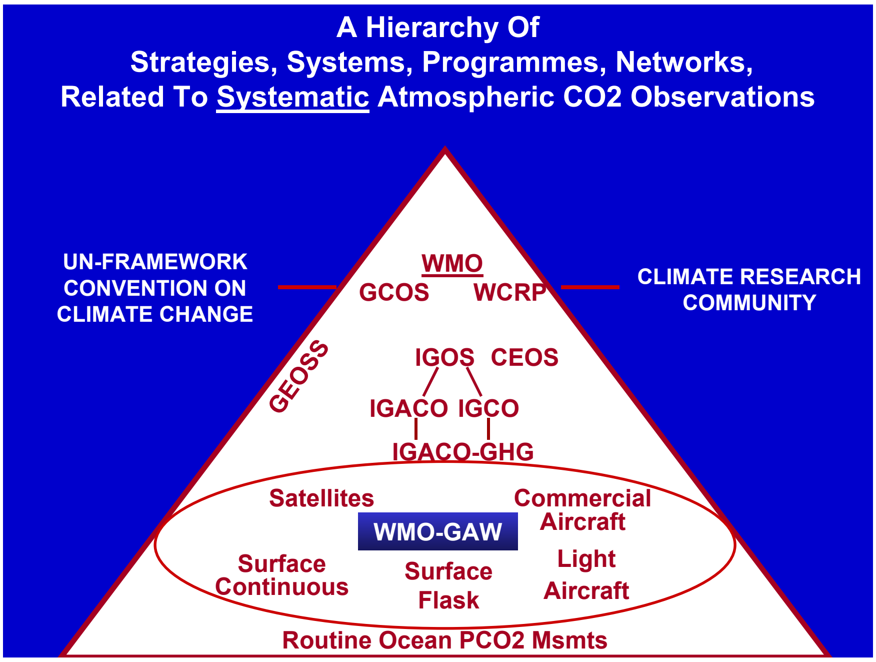

Figure 4: **The hierarchy of international activities related to promoting, organizing and conducting systematic atmospheric observations of carbon dioxide and other greenhouse gases. The foundation for this system are networks and facilities operated by leading countries in the field in cooperation with many other countries. The leaders include US/NOAA, Australia, Canada, China, France, Finland, Germany, Japan and Switzerland.**

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WORKSHOP PROCEEDINGS

All oral presentations and national reports given during the workshop are available online for download at http://www.wmo.ch/web/arep/gaw/gawreports.html

EXPERT GROUP RECOMMENDATIONS

The scientists present at the 13th WMO/IAEA Meeting of Experts on Carbon Dioxide Concentration and Related Tracers Measurement Techniques, September 19-22, 2005 in Boulder, CO, U.S.A., recommend the following procedures and actions, in order to achieve the adopted WMO goals for global network comparability among different laboratories and various components as summarised in Table 1. The term "network precision" used in earlier recommendations has been replaced by the term "network comparability". Definitions of terms concerning precision, accuracy etc. are given in Table 2.

Table 1: **Recommended inter-laboratory (network) comparability of components discussed.**

Component	Inter-Laboratory comparability
CO_2	± 0.1 ppm (± 0.05 ppm in the southern hemisphere)
$\delta^{13}C\text{-}CO_2$	± 0.01 ‰
$\delta^{18}O\text{-}CO_2$	± 0.05 ‰
$\Delta^{14}C\text{-}CO_2$	± 1 ‰
O_2/N_2	± 1 per meg
CH_4	± 2 ppb
CO	± 2 ppb
N_2O	± 0.1 ppb
H_2	± 2 ppb

Table 2: **Definitions of terms related to data quality.**

Term	Definition	~~R~~Ref.
Accuracy (of a test method)	The closeness of agreement between a test result and the accepted reference value.(a)	[1
Comparability	Mean difference between two sets of measurements, which should be within given limits.(b)	
Bias	The difference between the expectation of the test results and an accepted reference value.	[2
Precision	Degree of internal agreement among independent measurements made under specific conditions.(c)	[2
Repeatability (of results of measurements)	Closeness of the agreement between the results of successive measurements of the same measure and carried out under the same conditions of measurement.(d)	[2
Reproducibility (of results of measurements)	Closeness of the agreement between results of measurements of the same measure and carried out under changed conditions of measurement.(d)	[2
Uncertainty (Standard uncertainty)	A parameter associated with the result of a measurement that characterises the dispersion of values that could reasonably be attributed to the measurement.(e,f) (Uncertainty of the result of a measurement expressed as a standard deviation)	[2 [3

(a) Note that accuracy and precision are qualitative concepts and should be avoided in quantitative expressions.

(b) 1. For example, difference in a comparison of measurements of a species in a discrete sample with the hourly average for the same hour in which the discrete sample was collected. 2. In the case of significantly different variances of the two sample sets, the difference of the mean may not be meaningful. The Wilcoxon-Mann-Whitney test can be used to test for statistical significance.

[c] Precision must not be confused with accuracy or trueness. It is a measure for the dispersion of values.
[d] Repeatability and reproducibility may be expressed quantitatively in terms of the dispersion characteristics of the results. In practice quantitative expressions of repeatability or reproducibility often refer to a dispersion of ± 1 standard deviations.
[e] The concept of "uncertainty" is explained in detail in ISO Publications 1995.
[f] In practice the term "error (measurement error)" seems to be often used when actually "uncertainty" is meant. An error is viewed as having two components, a random and a systematic component. As further stated in ISO Publications (1995), "error" is an idealised concept and errors cannot be known exactly. "Error" and "uncertainty" are not synonyms, but represent completely different concepts.
Ref. 1, 2, 3: ISO Publications 1993a & b; 1995.

R1. CO_2 CALIBRATION

R1.1 Background

Round-robin comparisons of laboratory standards and comparisons of field measurements and samples over the last decade have regularly shown differences larger than the target comparability for merging data from different field sites (see Table 1). These systematic differences contribute to uncertainties in the location and magnitude of surface fluxes derived from atmospheric composition measurements. A CO_2 Central Calibration Laboratory (CCL) remains one of the fundamental components of the WMO strategy for addressing these problems.

R1.2 Requirements for the CO_2 Central Calibration Laboratory

a) The CCL maintains the WMO Mole Fraction Scale for Carbon Dioxide in Air by carrying out regular determinations of this primary scale with an absolute method at approximately annual intervals. The primary scale shall range from approximately 180 ppm (covering atmospheric values in ice cores) to over 500 ppm (expected atmospheric background values in the latter part of the 21st century). The scale is currently embodied in a set of 15 CO_2-in-air mixtures in large high-pressure cylinders (called “WMO Primary Standards”).

b) The CCL carries out comparisons with independent primary scales, established either through gravimetric, manometric, or other means. Since the WMO scale was maintained until 1995 by the Scripps Institution of Oceanography, comparisons with SIO are especially relevant because there are still some issues to be resolved. Comparisons with a gravimetric scale developed by the National Institute for Environmental Sciences in Tsukuba, Japan, and a manometric scale developed by the Institute of Ocean Sciences, in Sidney, BC, Canada, are encouraged.

c) The CCL will update its scale when warranted, as the CO_2 mole fractions of the WMO Primary Standards become better known over time through repeated absolute measurements and comparisons. Revisions of the WMO Scale by the CCL must be distinguished by name, such as WMO X2005. The CCL archives all earlier versions of the WMO scale.

d) The CCL provides complete and prompt disclosure of all data pertaining to the maintenance and transfer of the primary scale to the measurement laboratories participating in the WMO Global Atmosphere Watch (GAW) Programme.

e) The CCL provides calibrated reference gas mixtures of CO_2-in-air (called “transfer standards”) at the lowest possible cost.

f) The CCL provides for a backup in case a catastrophic event occurs.

g) In order to make possible a level of consistency among the CO_2 calibration scales of laboratories participating in the WMO GAW programme of ±0.03 ppm or less, the CCL shall aim to provide the calibrated standards for transfer of the primary scale to secondary and tertiary standards at that level of consistency.

h) The CCL, or a designated WMO World Calibration Centre, organizes round-robin comparisons of laboratory calibrations by distributing sets of high-pressure cylinders to be measured by participating laboratories. The round-robin comparisons are to be used for an assessment of how well the laboratories are maintaining their link to the WMO Mole Fraction Scale. They are not to be used for re-defining laboratory calibration scales, because that would effectively establish two or more traceable paths to the primary scale instead of a single hierarchical path. It is recommended that round-robins are repeated once every two years. However, comparisons of reference gases by themselves are not sufficient to ensure that atmospheric measurements are comparable to the degree that is required (see Section 9).

i) In order to assure comparability of round-robin results, circulation of cylinders is discontinued after two years at latest, and results are evaluated even if not all labs were able to yet analyse the tanks. A new round-robin will then be started with the labs that had not been included before to be first in line. Tracking tank circulation and data submission will be more rigorous than in earlier round-robins with the status of tank circulation and data submission being posted online on a Web Page to be installed and maintained by CMDL. People are encouraged to measure multiple species if time (4 weeks) and air consumption allow for.

R1.3 Maintenance of Calibration by GAW Measurement Laboratories

a) All laboratories that participate in the GAW programme must calibrate and report measurements relative to a single carefully maintained scale, the WMO Mole Fraction Scale for Carbon Dioxide in Air, including its version number. Each GAW measurement laboratory must actively maintain its link to the WMO Scale by having its laboratory standards re-calibrated by the CCL every three years. It is recommended that the laboratory primary gases are kept for many years so that a calibration history can be built for each of them.

b) It is recommended that each GAW measurement laboratory maintains a strictly hierarchical scheme of transferring the calibration of its laboratory primary gases to working standards, and from working standards to atmospheric measurements. Traceability via a unique path will, in principle, enable the unambiguous and efficient propagation of changes (including retro-active changes) in the assigned values of higher level reference gases all the way to measured values for atmospheric air.

c) In order to minimise the risk of creating offsets that are coherent among laboratories within the same region, each laboratory should maintain the shortest possible direct link to the WMO Primary Standards.

d) Because of ongoing improvements in measurement technology it is possible that individual laboratories or groups of laboratories may be able to maintain excellent precision and comparability in scale propagation from their laboratory standards to lower level standards, which could be beyond the precision with which laboratory standards can be tied to the WMO scale. Internal scales of this sort must also remain tied to the WMO scale to the extent possible.

R1.4 Improving Links to Primary Reference Materials

a) While the WMO scale is defined and maintained by an operational designated CCL, WMO and IAEA welcome efforts that monitor, confirm, or improve CCL links to primary reference materials or fundamental constants. Such efforts should involve cooperation with National Metrological Institutes (NMI).

b) In such cases, the WMO and IAEA Expert committees undertake the responsibility for the evaluation of the effectiveness of such measures and for recommending modifications to existing protocols.

R2. CO_2 STABLE ISOTOPE CALIBRATION

A number of intercomparison exercises have been conducted and reported on during the 13th WMO Meeting of CO_2 experts (see the contributions by Mukai, Huang and Brand with co-workers in this volume). These intercomparisons are representative for the state of the art in stable isotope ratio measurements on CO_2 in air. The intercomparison results allow to draw a number of conclusions as to possible reasons for measured isotopic differences between participating laboratories. The efforts themselves evolved into a valuable tool for early detection of trends and offsets of individual laboratories and set a new standard in calibration throughout a larger community of laboratories. The implementation of larger intercomparison efforts as a routine surveillance and quality control tool is strongly endorsed.

The following list reflects the results, discusses possible experimental and organizational consequences and provides the corresponding recommendations:

a) The possible experimental reasons for systematic offsets in measured CO_2 isotopic compositions differ for $\delta^{13}C$ and $\delta^{18}O$. In $\delta^{13}C$ scaling errors seem the most prominent issue whereas $\delta^{18}O$ suffers from exchange of oxygen with water as well as from different techniques of generating CO_2 from carbonate reference material.

b) The possible underlying causes must be addressed separately for clean (pure) CO_2 and for CO_2 in air. Clean CO_2 is developed from carbonates or is available as a calibrated clean gas. In contrast, CO_2 in air is always accompanied by N_2O. In addition, traces of co-trapped air from the cryogenic separation as well as issues of trapping efficiency and isotopic alterations during trapping can change the measured isotopic ratios.

c) There is only one internationally recognized isotope scale for $\delta^{13}C$: VPDB. This scale has recently been refined by IUPAC and IAEA. The origin of the scale remains defined thro NBS19 (= +1.95 ‰); in addition, a consensus value has been introduced by fixing the □^{3}C value of L-SVEC (Li_2CO_3) to –46.6 ‰ versus VPDB. Thus, the former 1-point scale has been complemented with a 2nd scaling point. As a result, a larger number of international secondary reference materials must be newly evaluated on the unified scale, including reference materials that have been used for CO_2-in-air isotopic calibration (see e). Intercomparability of $\delta^{13}C$ values of air-CO_2 in the past has mainly suffered from different cross contamination during mass spectrometric measurement (eta-effect). The new scaling rule should be able to adequately address this problem.

d) Since $\delta^{13}C$ of CO_2 in air is close to –8 ‰ on the VPDB scale, any secondary reference material used for high precision isotope work around this value needs to be reconsidered. The generation of two clean CO_2 reference materials (NARCIS 1 and 2) by NIES with a composition of NARCIS 1 close to air-CO_2 and NARCIS 2 close to NBS 19 has greatly facilitated intercomparison of isotope measurements on pure CO_2 from different laboratories. For establishing a set of recommended values from the intercomparison more data are required for NARCIS 2. MSC, NIES and MPI-BGC are asked to complete the examination and suggest recommended values at the 14th WMO Meeting of CO_2 Experts.

e) The availability and careful calibration of other CO_2 reference materials from NIST (carbon dioxide: RM 8562-8564) has proven to be an independent and reliable resource for tracing offsets between individual laboratory scales. Theses reference materials have already been reassessed on the 2-point VPDB scale with very small changes to the original values (i.e. RM 8562: $\delta^{13}C$= -3.72‰, RM 8564: $\delta^{13}C$= -10.45‰, RM 8563: $\delta^{13}C$= -41.59‰ (Coplen et al., 2006)).

f) Recent findings of the water-body related fractionation laws for $^{18}O/^{16}O$ and $^{17}O/^{16}O$ require a new ruling for high precision calibration of $\delta^{13}C$ in air-CO_2. It is recommended to adopt the ratio assumption set provided by Assonov and Brenninkmeijer (2003a, 2003b) with a fractionation coefficient of 0.528 and a $^{17}O/^{16}O$ ratio of 0.00038672 for VSMOW (corresponding to 0.00039511 for VPDB-CO_2). Mass spectrometry evaluation software as well as individual laboratory software packages should be adapted correspondingly.

g) Past laboratory intercomparisons (like the 'CLASSIC' experiment) have revealed that high precision isotopic results can be obtained reliably by comparing air samples directly or by extracting CO_2 and comparing to a pure gas reference. Both ways of calibration provide similarly precise results. Discrepancies between calibrations based on CO_2 versus those based on whole air reference materials are still observed. Future intercomparison exercises should be designed to eliminate this discrepancy.

h) The long term integrity of CO_2-in-air isotope results should be based on carbonate material. The initiative of MPI-BGC Jena of preparing CO_2 from carbonate material and mixing it with CO_2-free air in a fully automated system has made air reference material ('J-RAS', Jena Reference Air Set) available that closes a gap in the intercomparability and provides a firm link of air-CO_2 measurements to the VPDB scale (Ghosh et al., 2005). In addition to local scale generation it is recommended that participating laboratories should obtain a J-RAS set from Jena, calibrate the local working reference air and report isotopic results on the so obtained scale in addition to their usual way of reporting in intercomparison efforts. In turn, BGC Jena is asked to continue the production of the reference material for the community and provide further service by mixing local reference-CO_2 into CO_2-free air upon request.

i) The need of a calcite reference material with carbon and oxygen isotopic compositions close to atmospheric CO_2 is reiterated and emphasized. The material is necessary in order to eliminate ambiguities arising from different mass spectrometric scaling factors and other corrections (^{17}O correction, N_2O correction etc.).

j) Comparability of $\delta^{18}O$ data between laboratories remains poor (progress has been made with inter-laboratory precision of close to ±0.2 ‰, which is still far off the goal of ±0.05 ‰). The major cause for the discrepancies is not scaling (like for $\delta^{13}C$) because air-CO_2 is close to VPDB-CO_2. Further progress evidently cannot be made by having the individual laboratories generate CO_2 from NBS19 (and NBS18, as required for scaling to comply with the VSMOW/SLAP scale). Instead it is recommended to follow a master laboratory with the proven ability to generate CO_2 from carbonate material with a high long term precision record. MSC, NIES and MPI-BGC are asked to take the initiative and provide reference air with the CO_2 reliably calibrated for $\delta^{18}O$ on the (2-point) VPDB scale. Moreover, the link should be firmly established to the VSMOW $\delta^{18}O$ scale as well.

k) CSIRO-MAR is asked to provide a new suite of measurements of the CLASSIC cylinders taking the new scale issues (points d, f and i as well as j) into close consideration and prepare a report for the next CO_2 Experts meeting.

R3. RADIOCARBON IN CO_2 CALIBRATION

Radiocarbon (^{14}C) observations in atmospheric CO_2 are gaining increased interest in carbon cycle research, in particular for budgeting regional fossil fuel CO_2 contributions/emissions. Standardisation of Radiocarbon analysis has been well established in the Radiocarbon Dating Community for many years, and the New Oxalic Acid Standard (NIST SRM 4990C) has been agreed upon as the main Standard Reference Material. Other reference material of various origin and ^{14}C activity is available and distributed by e.g. IAEA.

In the atmosphere, recent $\Delta^{14}C$ gradients (north versus south in the free troposphere and marine vs. continental within hemispheres) are very small and on the order of general measurement precision, i.e. only several permil up to very few percent. Moreover, the “detection limit” to derive regional fossil fuel contributions even with the highest measurement precision is only about 1 ppm. Keeping the small atmospheric $\Delta^{14}C$ signals in mind, we, therefore, suggest a goal of 1 per mil or better for $\Delta^{14}C$ measurement precision and comparability between different laboratories. This translates to a fossil fuel detection capability of approximately 0.5 ppm CO_2 when $^{14}CO_2$ measurements from multiple facilities are used together. Although the repeatability of $^{14}CO_2$ measurements may be in the range of 2-5 per mil, it is still possible that comparability between different labs could be tracked at better than the 1 per mil. Prior experience of analyzing graphite derived from the same air at different Accelerator Mass Spectrometry (AMS) facilities, shows that while precision was estimated to be 2-3 per mil, mean inter-laboratory comparability was of order 0.2 per mil. An intercomparison activity dedicated to ^{14}C laboratories participating in atmospheric $^{14}CO_2$ monitoring is, therefore, strongly recommended. Tracking at the 1 per mil level could be achieved through the long term measurement of a common set of gases circulated between participating laboratories.

R4. O_2/N_2 CALIBRATION

A small community of twelve laboratories around the world are making high-precision atmospheric O_2/N_2 measurements. Currently there exists no common calibration scale, and small-scale intercomparison efforts have been undertaken by only a few laboratories. At the 12th WMO

CO_2 Experts Meeting, it was agreed that there was an urgent need to improve intercomparison efforts, as well as either working towards a common calibration scale, or at least establishing strong constraints linking the existing different scales.

Therefore, in 2004, the “GOLLUM” programme (**G**lobal **O**xygen **L**aboratories **L**ink **U**ltra-precise **M**easurements) was initiated, run by Ralph Keeling (SIO) and Andrew Manning (UEA). There are two components to this programme, a “sausage flasks” intercomparison programme, and a “round robin cylinder” intercomparison programme, as described in the previous WMO Recommendations Annex (WMO Technical Document No. 1275). Since not all O_2/N_2 laboratories are set up to analyse flasks, the round robin cylinder programme is vital to compare all laboratories. In addition, the two programmes assess different analytical aspects: The sausage flask programme intercompares a laboratory’s ability to extract and analyse air from a small flask sample, whereas the round robin cylinder programme essentially intercompares a laboratory’s calibration scale, and their methods for extracting air from high pressure gas cylinders. Since methodologies used to extract air from flasks or from high pressure cylinders are very different from each other, involving different analytical equipment, these two intercomparison programmes necessarily complement each other.

The round robin cylinders (2 sets of 3 aluminium cylinders) were prepared in 2004 at Scripps Institution of Oceanography, and started their worldwide rotations in 2005. At the time of the 13th WMO Experts meeting, there were not enough results to derive any conclusions. The cylinder rotations will continue indefinitely, and the data will be reported at the 14th WMO Experts meeting. One round of sausage flasks were distributed and analysed in 2004, and a further set in 2005. Again because of the small amount of data, it is premature at this stage to derive conclusions. Because of the difficulty ensuring that all flasks filled in a sausage chain (some of which necessarily are at different pressures) contain exactly the same O_2/N_2 ratio, the value of the flasks programme to the community is uncertain. We hope to evaluate this in more detail at the next Experts meeting. Preliminary results from the round robin cylinder programme are more encouraging, however.

Since the last Experts meeting, we are no closer to establishing an O_2/N_2 CCL, and there will likely be no change to this situation in the foreseeable future. For this reason, it was agreed that the GOLLUM round robin cylinders could potentially be used to define a provisional global O_2/N_2 calibration scale. This depends on at least three points:

a) The O_2/N_2 ratios in the GOLLUM cylinders are proven to be stable over time. This will be assessed upon their return and reanalysis at Scripps Institution of Oceanography, expected approximately 18 months after the start of the round robin, and will be continually assessed each time the cylinders return to SIO.

b) In contrast to the CO_2 community, the O_2/N_2 community uses several different analytical techniques to measure and report O_2/N_2 ratios. This fact must always be kept in mind when comparing data, for example, because of differences in interference effects from other trace gas species.

c) Additional intercomparison efforts should continue to be made between various O_2/N_2 laboratories, so that the community is not entirely dependent on the GOLLUM cylinders. In addition to the occasional GOLLUM sausage flasks, examples are: SIO and Princeton University shared flask sampling sites (CGO, SMO); SIO and MPI-BGC Jena shared flask sampling site (ALT); CarboEurope-IP shared flask sampling site (planned: LUT); CarboEurope “cucumber” cylinder round robins.

As a related point, we note that an increasing number of laboratories have purchased a very small set of “primary calibration cylinders” from the Scripps Institution of Oceanography. Such a small set of cylinders is not sufficient to maintain any laboratory’s calibration scale, but it can serve to assist in establishing a common calibration scale.

R5. CH_4 CALIBRATION

R5.1 Background

At the 12th WMO/IAEA Meeting of Experts on Carbon Dioxide Concentration and Related Tracers Measurement Techniques, September 15-18, 2003 in Toronto, Canada, there was general agreement that a gravimetrically-prepared standard scale developed at NOAA CMDL would define the WMO GAW primary CH_4 mole fraction scale, and that NOAA would assume the role of the Central Calibration Laboratory (CCL) for methane. This new scale, designated NOAA04, covers the nominal range of 300 to 2600 nmol mol^{-1}, so it is suitable to calibrate standards for measurements of air extracted from ice cores and contemporary measurements from GAW sites. This new scale results in CH_4 mole fractions that are a factor of 1.0124 greater than the previous scale (now designated CMDL83) (Dlugokencky et al., 2005).

R5.2 Requirements for the GAW CH_4 CCL

a) NOAA will maintain a gravimetrically-prepared CH_4-in-air standard scale covering a range of CH_4 mole fractions of interest to our community.
b) The CCL carries out comparisons with independent primary scales, including the national metrology laboratories.
c) The CCL provides complete and prompt disclosure of all data pertaining to the maintenance and transfer of the primary scale to the measurement laboratories participating in the WMO Global Atmosphere Watch (GAW) Programme.
d) The CCL provides calibrated mixtures of CH_4-in-air at the lowest possible cost.
e) The CCL provides for a backup in case a catastrophic event occurs.
f) The CCL will transfer the primary scale to calibrated CH_4-in-air standards with an uncertainty of <1 nmol mol^{-1}.

R5.3 Maintenance of Calibration by GAW Measurement Laboratories

a) All laboratories that participate in the GAW programme must calibrate and report measurements to the World Data Centre for Greenhouse Gases relative to the WMO CH_4-in-air mole fraction scale. Each GAW measurement laboratory must actively maintain its link to the WMO Scale by having its highest-level standards re-calibrated by the CCL every five years. It is recommended that laboratory primary standards are used only to calibrate working standards so that a calibration history can be built for each of them.
b) Each GAW measurement laboratory should maintain a strictly hierarchical scheme of transferring the calibration of its primary standards to working standards, and from working standards to atmospheric measurements. Traceability along a unique path will enable unambiguous and efficient propagation of changes (including retro-active changes) in the assigned values of higher level standards to atmospheric measurements.
c) Each laboratory should maintain the shortest possible direct link to the WMO Primary Standards.

R5.4 Improving Links to WMO Primary Standards and Primary Reference Materials

a) The CCL or a designated WMO Calibration Centre organises round-robin comparisons of laboratory calibrations by distributing sets of high-pressure cylinders to be measured by participating laboratories. The round-robin comparisons are to be used for an assessment of how well the laboratories are maintaining their link to the WMO CH_4 Mole Fraction Scale. They are not to be used for redefining laboratory calibration scales. We recommend that round-robins are repeated once every two years. However, comparisons of standard gases alone are not sufficient to ensure that atmospheric measurements are comparable to the degree that is required (see Section 9).

b) While scales can only be defined and maintained by a designated CCL, WMO and IAEA welcome efforts that monitor, confirm, or improve CCL links to primary reference materials or fundamental constants. In such cases, the WMO and IAEA Expert committees undertake the responsibility for the evaluation of the effectiveness of such measures and for recommending modifications to existing protocols.

R6. CO CALIBRATION

R6.1 Background

CO is an important component in tropospheric chemistry due to its high reactivity with OH. It is the major chemically active trace gas resulting from biomass burning and fossil fuel combustion and a precursor gas of tropospheric ozone. Most measurements are based on *in-situ* analysis or that of collected air samples. The NOAA/CMDL air (flask) sampling network provides a large and systematic set of globally distributed surface observations. *In-situ*, ground based measurements provide the high temporal resolution not achieved through other measurements. Observations made during aircraft campaigns form the second most important database, and combined with other measurements, are used to study atmospheric chemical processes. Differences among reference scales have been an ongoing problem for CO measurements. Spectroscopic retrieval of CO provides column abundances. Wide geographical coverage of CO with some limited vertical resolution is becoming available from several satellite-based sensors (MOPITT-TERRA, SCIAMACHY-ENVISAT, TESS-AURA).

R6.2 Analytical Techniques and Problems

The present recommendations solely pertain to the calibration of non-remote sensing methods. The validation of remote sensing data is a complicated separate issue not treated here. Experience has shown, however, that even the accurate calibration of CO measurements based on chemical/physical methods is far from trivial. Mole fractions between 40-250 nmol/mol should be determined with an uncertainty of ± 1 ppb.

Unlike CO_2, for CO there is a low degree of standardisation in analytical techniques deployed. There are in fact at least six analytical techniques in use. In (estimated) order of frequency of usage: 1) gas chromatography using a reduction gas detector (GC-HgO), 2) gas filter correlation, 3) vacuum ultraviolet fluorescence (VUV), 4) gas chromatography using methanization and a flame ionisation detector, 5) Tunable Diode Laser Absorption Spectroscopy, and 6) absolute volumetric determination. The last 2 methods require custom-made instrumentation and are relatively rare. VUV is becoming increasingly available through a commercial instrument that provides a linear response from atmospheric CO levels through to ~ 10 ppm.

The specific calibration problems for CO are: a) gravimetric mixtures must be diluted to environmental levels, which introduces errors, b) at these levels CO mixing ratios in storage containers are not stable over time periods of years or longer, and c) the most available measurement techniques do not have the stability or precision for long-term measurements of low rates of drift. NOAA/CMDL's Carbon Cycle Group has on two occasions organised round-robin tests involving 5 to 10 laboratories. This has helped "the international CO community" enormously, but also exposed some drift and inconsistency in the NOAA/CMDL calibration scale.

It is noted that like for CO_2, CO mixing ratios in gas storage cylinders may change with time. The preparation of a gravimetric standard does not *a priori* guarantee that the actual CO mixing ratio corresponds to the assumed one. There are two ways around this problem, namely either more extensive research in understanding the problems of stability of CO in storage cylinders, or volumetric measurements. The Max-Planck-Institute for Chemistry, Mainz, Germany, the only laboratory making volumetric measurements of CO, has discontinued the programme due to lack of resources.

WMO through the EMPA has endeavoured to improve the international situation implementing an audit system for CO measurements at GAW stations. Combining all experience gained so far, it is realistic to expect CO data to be expressed on one single scale that is traceable to a single source. Nonetheless, an independent verification through an absolute volumetric determination procedure is desired. A realistic target for the standard uncertainty of measurements is at the 1% level. For establishing global trends, and to get a sufficiently accurate estimate of the tropospheric burden, it seems that 1% is now becoming both analytically attainable and scientifically sufficient.

R6.3 Recommendations

a) Inter-laboratory comparability to ±2 ppb and standards to ±1 ppb are needed. Comparisons of CO measurements among laboratories (through round-robins, and other intercomparison sample exchanges) have documented differences in measurements among laboratories. They have proven useful in identifying inconsistencies and/or drift in CO reference gases and therefore are strongly encouraged.

b) NOAA/CMDL is the CCL for carbon monoxide. In this capacity, they provide calibrated reference gases to GAW laboratories and CO calibrations should be traceable back to the scale maintained by NOAA/CMDL. Based upon several sets of gravimetric standards this scale was revised in 2000, and all measurements at GAW stations should refer to the most recent scale. The CCL is responsible for distributing of all revisions.

c) In order to be able to use CO as a tracer for fossil fuel CO_2 at regional GAW or even moderately polluted sites the CCL will extend its calibration scale towards higher mole fractions (up to 1000 ppb).

d) The WMO SAG for Reactive Gases should continue working to resolve issues of the calibration scale. Unfortunately, there is no laboratory currently conducting absolute volumetric measurements of CO. These measurements are extremely helpful in establishing the consistency and potential drift in the international scale. Both the Max-Planck Institute of Chemistry in Mainz and NOAA/CMDL are capable of making such measurements.

e) EMPA is the designated World Calibration Centre for Surface Ozone, Carbon Monoxide and Methane (WCC-EMPA) and is in charge of conducting system and performance audits including intercomparisons at global GAW stations. Audit results should be archived along with other CO data at the WDCGG. The scientific advisory group (SAG) for reactive gases has been established and their first focus is on carbon monoxide. A guidance document on CO measurements is being developed.

R7. N_2O CALIBRATION

R7.1 Background

Measurements of nitrous oxide are made by a number of laboratories around the world in order to better understand the sources and sinks of this greenhouse gas. Systematic differences between mole fractions reported by different laboratories are large compared to atmospheric gradients. The mean interhemispheric difference in N_2O mole fraction is around 1 ppb and the pole-to-pole difference is 2 ppb. These global differences are 0.3-0.6% of the recent mean mole fraction of N_2O in the atmosphere. This necessitates not only high measurement precision, but also high consistency among assigned values for standards. Inter-laboratory comparability of 0.1 ppb is needed.

R7.2 The NOAA N_2O Calibration Scale

NOAA serves as the CCL for nitrous oxide. The NOAA 2000 N_2O scale was developed in 2000 from 17 gravimetrically prepared compressed gas standards. This set of ppb-level standards consists of four standards prepared in 1993 (in 29-L Aculife-treated aluminium cylinders) and 13 standards prepared in 2000 (in 5.9-L untreated aluminium cylinders obtained from Scott-Marrin Inc.). These standards were derived from three different ppm-level standards, all of which were prepared from >99.9% N_2O (Scott Specialty Gases). All gravimetrically prepared standards contain CO_2 (330-380 ppm) and SF_6 (1-40 ppt). Because the 1993 standards are nearly depleted, new standards are being prepared to replace them. A scale update was released in July 2006. The new NOAA-2006 scale is 0.17 ppb lower than the 2000 scale at 320 ppb (see www.cmdl.noaa.gov/hats/standard/n2O_scale.htm).

In 2002, an Agilent 6890 gas chromatograph was configured for N_2O/SF_6 analysis using CO_2-doped nitrogen as carrier gas. The precision of the Agilent/N_2 system has proved to be better than that of the previously used Valco/P5 system (which used a Valco ECD with 95% argon / 5% CH_4 carrier gas). More importantly, this instrument has proved to be more stable over changes in operating conditions and carrier gas. This instrument change improved NOAA's ability to provide consistent N_2O calibrations.

At NOAA, primary standards are prepared gravimetrically as described above. Secondary standards are dilutions of free tropospheric air obtained from Niwot Ridge, Colorado, USA, for which concentrations are determined by reference to the primary standard curve. Secondary Standards are used to calibrate Tertiary Standards for distribution to NOAA sites and laboratories. It is the NOAA Tertiary Standards that are used as Laboratory Standards by the World Calibration Centre (WCC) and any participating laboratories.

Currently, NOAA maintains its scale by analysing 13 primary standards annually, and five secondary standards over the 260-350 ppb range twice per month. A second working standard (318 ppb) is run weekly as a secondary check on uncertainties. Precision (1 standard deviation) normally varies between ± 0.06 and ± 0.3 ppb. Current reproducibility (95% C.L.) is 0.2 ppb at ambient mixing ratios and 0.3 ppb at 260 and 350 ppb.

R7.3 Recommendations for Participating Laboratories and Field Sites

For most N_2O systems, the repeatability (1 standard deviation) of the gas chromatographic method under ambient sampling is expected to be better than ± 0.5% (± 1.5 ppb). A value of at least ± 0.1% (± 0.3 ppb) should be aimed at for all GAW stations. With high-quality equipment, a precision corresponding to ± 0.04% (± 0.15 ppb) can be achieved. Precision should be determined from multiple, interspersed analyses of a gas of constant N_2O mole fraction (e.g. working standard) during routine operation.

A set of laboratory standards with at least five different N_2O mole fractions calibrated by the CCL (NOAA) should be obtained by each GAW station and should serve as the station's highest-level standards. These are to be safeguarded, used only for infrequent calibrations of working standards or reference gas, and they should be recalibrated by the CCL every 5 years. Working standards at each laboratory can be either appropriately prepared synthetic gas mixtures or dried ambient air compressed into high-pressure aluminium cylinders. Besides N_2O, synthetic mixtures should contain atmospheric levels of N_2, O_2, and CO_2 as a minimum. For the use at a GAW station these should be calibrated by comparison with the station's set of laboratory standards or an equivalent set of standards traceable to the NOAA scale.

For basic calibration of the analytical system and for intercomparison, standards with five different N_2O mole fractions ranging between 290 and 350 ppb should be used. This will determine the response curve of the ECD. These standards should be compared with laboratory standards (calibrated by the CCL) at least twice a year. It is recommended to run analyses of samples of assigned N_2O mole fraction from a "target cylinder" once per day or more frequently. This will enable early detection of minor malfunctions of the analytical system. These and other analytical and quality control procedures are discussed in detail in the Measurement Guidelines / Data Quality Objectives for N_2O, which are currently being edited by the SAG GG (Report in preparation).

R8. H_2 CALIBRATION

R8.1 Background

Hydrogen plays a significant role in global atmospheric chemistry due to its interference in CH_4-CO-OH cycling. The balance of hydrogen could change with the implementation of a new H_2 energy source. Therefore it is important to establish its global budget and atmospheric trend.

There is currently no internationally accepted standard scale available for measurements of atmospheric hydrogen nor is there any institution to distribute such standards. Existing measurement data are reported relative to internal scales of the respective laboratory. Offsets between the individual scales are mostly not known, nor are any non-linear (concentration dependent) deviations; also the relative stability of different scales over time has not yet been assessed. A long term intercomparison experiment performed by NOAA-CMDL and CSIRO with Cape Grim flask samples revealed that differences between the labs were not constant. A solid evaluation of atmospheric H_2 trends using measurements from different programs would be difficult to achieve at present.

R8.2 Recommendations

a) The NOAA-CSIRO intercomparison experiment has proven a very useful tool to get information on the comparability of atmospheric data. There are several existing ICP that are encouraged to include H_2 in order to check for the comparability of respective data sets. Experience has shown that H_2 in aluminium cylinders may drift. Therefore round-robins using containers suitable for H_2 are encouraged.

b) The main problem most laboratories that measure hydrogen encompass is to ensure the stability of their reference gases. Commonly used aluminium cylinders for other trace gas standard mixtures often show significant growth of hydrogen and are therefore useless as hydrogen standards. However, there also exist cylinders of the same type that have much better properties in that respect without the reason being understood. Major effort should be undertaken to find out how to improve properties of the cylinders. Stainless steel containers from Essex Cryogenics have been tested successfully.

c) The development of reference gases by independent laboratories is encouraged. The effort to establish gravimetric scales has led to very infrequent updates. A less tedious procedure to regularly check the stability of a scale should be pursued.

R9. GENERAL RECOMMENDATIONS FOR QUALITY CONTROL OF ATMOSPHERIC CO_2 MEASUREMENTS

R9.1 General

a) Relating standards to the WMO CO_2 Mole Fraction Scale: Investigators should follow practices outlined in Section 1.3 of this report for obtaining a sufficient number and range of calibration gases from the WMO CCL (laboratory standards) and transferring those calibrations to working and field standards. Data management system should allow for easy reprocessing and easy propagation of scale changes from primary laboratory standards to final measurements.

b) Real-air and modern-CO_2 standards: Working standards must have natural levels of N_2, O_2, and Ar to avoid biases due to different pressure-broadening effects between sample and calibration gases. Standards should have CO_2 with ambient $\delta^{13}C$ ratios.

c) Besides round-robin comparisons, more frequent intercomparison activities between pairs of laboratories which incorporate the analyses of actual air samples, such as flask air intercomparison (ICP) experiments or collocated in-situ instruments are strongly recommended. The tremendous benefit of routine intercomparison has been demonstrated (Masarie et al., 2001) and is reinforced. Mutual exchange of air in glass flasks is encouraged as a means to detect experimental deficiencies at an early stage and remove discrepancies in the results quickly.

d) Flask sampling programs should be implemented at observational sites making continuous measurements as well as automated data processing for these intercomparison projects. A detailed comparison of collocated continuous and flask measurements will be performed until the next WMO Experts meeting which will form the basis to assess the usefulness of such a programme and to decide if a WCC is needed also for CO_2 in order to perform audits at GAW stations.

e) Clear protocols and reports of experience gained in intercomparison projects should be provided. Results should be published in the peer-reviewed literature. The evaluation of such activities and recommendations for refinement, co-ordination and expansion of such activities has been accepted as a key responsibility of future WMO/IAEA Expert meetings.

f) Defensible uncertainty estimates: Investigators should report uncertainty estimates for their data and provide details of how these estimates are calculated and what activities are used to verify them. ISO nomenclature shall be used for uncertainty estimates and discussions.

g) Deviations from recommendations: We recognize the value of innovation and experimentation with new approaches. However, we stress that any deviations from established practices should be fully tested to confirm that the new approach does not introduce bias into the measurements. Furthermore, the results of such experimentation should be reported at future WMO CO_2 Experts meetings and similar venues, and published in the peer-reviewed literature whenever possible.

R9.2 Flask Measurements

a) Intercomparison programmes distributing to a larger number of laboratories flasks filled in series from tank air as a “sausage” as initiated by the European TACOS project (Levin et al., 2003) are able to increase the benefit of mutual flask exchange.

b) Another possibility to link several laboratories in one single intercomparison exercise is the establishment of Trace Gas Comparison Sites which will take on the task to fill a larger number of flasks regularly and simultaneously with ambient air and distribute them to participating laboratories. The Alert, Mauna Loa and Cape Grim stations have been recommended as such sites.

R9.3 In Situ Measurements

Continuous *in-situ* measurements of CO_2 can greatly improve our understanding of regional-scale carbon fluxes. For this reason, and in response to recent advances in technology, the number of investigators and sites carrying out in-situ CO_2 measurements is rapidly increasing. Many sound principles for conducting such in-situ CO_2 measurements have been described in detail in WMO GAW Report No. 134 (1999). Efforts have been initiated to update this report in the near future. To further support the integration of data from existing and new continuous measurement sites to the WMO-recommended inter-laboratory comparability standards, we make the following general recommendations.

a) The experts group recommends updating the CO_2 Measurement Instruction Manual (written by N. Trivett, 1999 GAW Report No.134) including examples for instrument solutions and providing a list of tests to be conducted to assure high performance of the system.

b) Drift in instrument sensitivity: Drifts in analyzer zero, span, and non-linearity should be characterized and an appropriate calibration scheme devised to correct for them at a level better than ±0.1 ppm. We recommend time intervals for zero, span, and non-linearity calibrations of half the amount of time it typically takes for drift in these parameters to lead to a 0.1 ppm bias. Calibration levels should bracket the range of observed concentrations and total one more calibration point than is necessary to determine the curvature of the instrument response (e.g. 4 points for a 2nd order curve fit).

c) Short-term instrument noise: Discrete sample and calibration measurements must be averaged over a long enough time to provide ±0.1 ppm measurement precision or better.

d) Instrument pressure sensitivity: If cell pressure is not actively controlled, the pressure sensitivity of the analyzer and its concentration dependence must be routinely measured.

e) Instrument temperature sensitivity: Analyzers should be located to the greatest extent possible in a stable temperature environment. If temperature is not actively controlled to a high level, the temperature sensitivity of the analyzer and its concentration dependence must be routinely measured.

f) Drying of air: Simultaneous H_2O concentration measurements are typically not sufficient to accurately compensate for interference, pressure-broadening, and dilution effects on the CO_2 measurement, and transient surface effects from wetting and drying tubing between sample and calibration gases can be significant. Therefore, adequate and verified removal of water vapour from sample gas to a dew point of at least -40°C is a requirement for in-situ CO_2 measurements.

g) Drying system altering CO_2 concentration: A cold trap can work well for drying and is unlikely to alter CO_2. Most chemical drying agents absorb CO_2 and are not suitable for use. Magnesium perchlorate can be used, but generally only under conditions of constant flow and pressure. Nafion driers also absorb or release CO_2 in response to pressure changes and should be maintained at constant flow and pressure: Careful analysis of potential transient effects following switches between calibration and sample gases should be carried out.

h) Flushing of cell and dead volumes: Flow rates should be fast enough and dead volumes minimized to allow for complete flushing of the sample cell at transitions between gases from different intake lines or reference cylinders. Multi-point calibrations should alternately be run in opposite order to look for incomplete-flushing artifacts. Also, tests should be performed that ensure that regulators are sufficiently flushed during a measurement cycle given the length of their stagnant period, operational flow rates, and regulator materials.

i) Leaks through fittings and valves: The negative impacts of small leaks to the laboratory environment or of calibration gas through solenoid valves necessitates frequent and automated leak checking. Even leaks at positive pressure can significantly bias CO_2 measurements through back-diffusion.

j) Whole-system diagnostics and comparability verification: It is essential that independent CO_2 observing systems and networks have means of verifying system performance and comparability. In addition to intercomparison activities (see above), gas from a surveillance cylinder (also known as a target gas) should be measured at different times of day and treated in data processing as an unknown. If possible, this gas should share a common path with sample gas through pumps, driers, and valve manifolds.

k) Automated data processing and diagnostic checks: Sites should have internet or modem connections to improve diagnostic and system repair capability, even though local technicians may be available on site. Emphasis should be placed on establishing automated data retrieval and processing systems to allow for near-real time data viewing and diagnostic checking. Automated electronic notification (e.g. email) of possible problems (examples could include pump and drier performance, flask vs. in-situ data comparisons outside set limits, computer event logs, data transfer logs etc.) is also recommended.

l) A routine data quality control strategy (e.g. monthly) and adequate data collection facilities as mentioned above, back-end processing, storage and backup should be implemented. It is recognized that a functional and automated data management strategy goes hand in hand with data quality (Section 10).

m) A highly available and qualified principle investigator (PI) as well as personnel backup support (for periods when PI or assigned technicians are on extended leave) should be ensured.

n) Adequate redundancy in key systems (spare analytical parts, computers and associated peripherals etc.) must be guaranteed.

R10. RECOMMENDATIONS FOR DATA MANAGEMENT AND ARCHIVING

R10.1 Data Management

All GAW measurement laboratories regardless of programme size are required to manage all new and existing atmospheric trace gas and supporting (meta) data using a database management strategy (DBMS) that meets or exceeds the following criteria:

a) Demonstrate that mole fractions / isotope ratios can be unambiguously and automatically reproduced from raw data at any time in the future.
b) Demonstrate that revisions to a laboratory's internal calibration scale can be efficiently and unambiguously propagated throughout the database.
c) Support routine and automatic database updates of all measurement and meta data.
d) Ensure that all data reside locally, in a single location, and are centrally accessible to internal users.
e) Ensure fast and efficient retrieval of all data.
f) Maximise users' ability to assess data quality.
g) Facilitate data exploration.
h) Minimise the risk of data loss or corruption due to theft, misuse, or hardware/software failure.
i) Maximise security to primary data (e.g., data from which all processed data is derived).
j) Support routine and automatic backup of all data.
k) Support complete data recovery in the event of catastrophic data loss.

GAW measurement laboratories are encouraged to use WMO/GAW Report No. 150 as a guideline in developing and implementing an atmospheric data management strategy.

R10.2 Data Archiving

a) Laboratories participating in the WMO-GAW programme must submit their data to the World Data Centre for Greenhouse Gases (WDCGG) regularly and promptly. A co-ordinated annual submission of data, with clearly identified version number of submitted data and calibration scale, as well as supporting details is strongly recommended. The same recommendation holds to other public-access data archive centres such as the Carbon Dioxide Information Analysis Centre (CDIAC).
b) For promoting early data submission and increasing data utilization, the WDCGG will publish a new version of the WDCGG Guide that includes new data categories, new data submission formats, data submission procedures, and distribution ways of data and products. The use of this WDCGG Guide is strongly recommended after it has been published.
c) The SAG-GG and WMO Secretariat coordinate harmonization of data management by WDCGG and NOAA GLOBALVIEW.
d) The WDCGG distributes data in versions consistent with the annual CD-ROM Report and keeps old versions.

R10.3 Co-operative Data Products

All laboratories making high-quality atmospheric carbon dioxide and methane measurements are strongly encouraged to participate in the Co-operative Atmospheric Data Integration Project which produces the GLOBALVIEW data products. The majority of current participants provide updates in May that include data through December of the preceding year. Data contributed to the GLOBALVIEW project are used to derive the data product. The product includes no actual data.

R11. SUMMARY OF RECENT INTERNATIONAL PLANNING OF ATMOSPHERIC TRACE GAS MEASUREMENT STRATEGIES

This report is prepared in the context of widespread governmental acceptance of climate change (United Nations Framework Convention on Climate Change (UNFCCC) and its Kyoto protocol), and leads to new and urgent challenges to the carbon cycle community. Two main objectives justify the deployment of atmospheric observations:

1. To quantify the present state of the fluxes of greenhouse gases and better understand the controlling processes.

2. To monitor and assess the effectiveness of emission control and/or reduction activities on atmospheric levels, including attribution of sources and sinks by region and sector.

International scientific planning has been co-ordinated by the Global Carbon Project (GCP) (http://www.globalcarbonproject.org/) combining the efforts of International Geosphere-Biosphere Project (IGBP), World Climate Research Project (WCRP) and International Human Dimensions Programme (IHDP). The GCP produced in 2003 a Science Implementation Plan dealing with the patterns and variability of carbon fluxes, the associated processes and feedbacks, and the management of the carbon cycle. GCP identified both systematic observations of concentrations in the atmosphere and oceans and process-oriented carbon cycle observations. In parallel, the Integrated Global Carbon Observing Strategy Partnership (IGOS-P) has formed a Theme Team called IGCO (Integrated Global Carbon Observation) to report on those systematic global carbon observational networks that can form the backbone of a future monitoring system, building upon earlier planning by GTOS/TCO (Terrestrial Carbon Observations http://www.fao.org/gtos/TCO.html) and GOOS (Global Ocean Observing System http://ioc.unesco.org/goos/). The IGCO Theme Team task is to establish data requirements, design network configurations, and develop advanced algorithms for carbon observations, which will be the core of a future, sustained observing system by 2015.

In both GCP and IGCO documents, a strong atmospheric observing component is outlined as indispensable to link land and ocean observing components and to integrate across spatial heterogeneities and temporal variability of local flux information. A modelling strategy for developing Carbon Cycle Data Assimilation schemes that will interpret observations in terms of fluxes is also outlined, based upon a combination of data and models for the different domains: atmosphere, ocean and land, where results from one domain place valuable constraints on the workings of the other two (“multiple constraint”).

Two major regional programmes have received funding to increase the density of atmospheric trace gas observations and terrestrial carbon observations over North America (NACP; http://www.esig.ucar.edu/nacp/) and Western Europe (CarboEurope-IP; http://www.carboeurope.org/). It is important that those regional programmes remain tightly linked to the international GAW effort and produce regional data sets that can be merged safely into an enhanced global picture of carbon sources and sinks.

Lessons from such regional initiatives should be valuable to formulate future atmospheric observing strategies for the remaining under-sampled regions, in particular in the tropics. The strong commitment to build-up of expertise in developing countries by WMO and IAEA, including the establishment of high-quality measurement capabilities, remains a critical issue for achieving adequate spatial coverage of the globe in the coming decade.

The following observational strategies seem to be most promising in this context:

a) Expand aircraft flights over vegetated areas not sampled or under-sampled, with priority to tropical South America, Africa, South East Asia. Higher altitude flights shall be needed to cope with vigorous convective mixing up to 10 km in the tropics. For that purpose, the use of passenger aircraft such as pioneered in atmospheric chemistry (CARIBIC, MOZAIC programmes) should be promoted.

b) Make the effort to recruit scientists from the under-sampled continents/areas to join the WMO Experts group.

c) Carry out continuous measurements in the boundary layer, in particular on top of high towers, and further pursue the option to use eddy flux towers as a platform for additional precise CO_2 mixing ratio observations (Bakwin et al., 2006). These observations will enable us to quantify regional sources and sinks by means of inverse modelling.

d) Develop and implement long-term measurements of total column Greenhouse Gases at a number of GAW sites recognising the need for Satellite calibration/validation and modelling.

e) Carry out in the vicinity of continuous tower-based boundary layer measurement sites frequent vertical profiles if possible under all weather conditions, which will quantify the vertical mixing of surface sources and sink fluxes.

f) Develop high-quality measurements of carbon cycle tracers that can be used to attribute natural fluxes to their controlling processes ($^{13}CO_2$, O_2/N_2, ^{18}OCO) and separate fossil fuel emissions ($^{14}CO_2$, CO…). Along these lines it is absolutely essential that detailed spatially and temporally resolved fossil fuel CO_2 and CO emissions inventories be developed and pursued.

g) Develop high-quality measurements of transport tracers (SF_6, ^{222}Rn, C_2Cl_4…) in order to validate numerical models of atmospheric transport (in particular their vertical mixing) including aircraft sampling.

h) Report actual uncertainties on individual data where available. In particular, pursue the development of data products (e.g. GLOBALVIEW) that can include wherever possible information on representativeness, calibration offsets, etc.

i) Plan atmospheric measurements jointly with terrestrial and oceanic process communities to optimise the link of atmospheric composition change to surface processes. For example, the development of the “virtual tall tower” concept to use short towers as part of atmospheric networks, and the synergetic use of ocean ΔpCO_2 survey programmes to make atmospheric measurements.

j) Encourage and facilitate the development of improved atmospheric tracer transport models. Among the identifiable needs are improving the representation of atmospheric convection, the representation of the surface boundary layer and the need to improve spatial and temporal resolution to better account for sources and sinks variability. Equally as important for assessing the distribution of fluxes is the use of several independently developed models and their frequent intercomparison. Finally, it is important to develop and maintain community models which are numerically efficient, which can run from standard computer platforms with a modest amount of training, and which are made available to the scientific community as a whole.

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ANNEX A

13th WMO/IAEA Meeting of Experts on Carbon Dioxide Concentration and Related Tracers Measurement Techniques

(Boulder, Colorado 19-22 September 2005)

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ANNEX B

PREVIOUS MEETINGS OF THE WMO EXPERTS IN CO_2 MEASUREMENT

The first meeting of the Experts on Carbon Dioxide Measurement was held in La Jolla, California, Unites States of America, and sponsored by the World Meteorological Organization (WMO). WMO has sponsored all subsequent meetings. These meetings have provided a quasi-regular communication among all national CO_2 monitoring programmes, which has ensured that CO_2 is monitored with the best current techniques available, that advantage is taken of new methodologies as they become available, and that all programmes are intercalibrated by accepted international standards.

The following is a list of meetings in this series:

	LOCATION	DATE	PUBLICATION
1.	La Jolla, California, USA	3-7 March 1975	4*
2.	Geneva, Switzerland	8-11 September 1981	6†
3.	Lake Arrowhead, California, USA	4-8 November 1985	39†
4.	Gaithersburg, Maryland, USA	15-17 June 1987	51†
5.	Hilo, Hawaii, USA	24-26 March 1988	‡
6.	Lake Arrowhead, California, USA	14-19 October 1990	77‡
7.	Rome, Italy	7-10 September 1993	88†
8.	Boulder, Colorado, USA	6-11 July 1995	121†
9.	Aspendale, Australia	1-4 September 1997	132†
10.	Stockholm, Sweden	23-26 August 1999	
11.	Tokyo, Japan	25-28 September 2001	148†
12.	Toronto, Canada	15-18 September 2003	161†
13.	Boulder, Colorado	19-22 September 2005	168

* Number of reports in the WMO Executive Panel-I/Document 5, 13.3.1975.

† Number of reports in the WMO Atmospheric Environment and Research Programme/GAW Report Series.

‡ Elliot, W.P. (ed.) (1989) The statistical treatment of CO_2 data reports. NOAA Technical memorandum ERL ARL-173.

ANNEX C

13th WMO/IAEA Meeting of Experts on Carbon Dioxide Concentration and Related Tracers Measurement Techniques
(Boulder, Colorado 19-22 September 2005)

Meeting agenda

Monday, September 19

8:00-9:00	Registration
9:00-9:10	Organizers Announcements
9:10-9:20	Welcome to Boulder/CMDL (James Butler, Deputy Director, CMDL)
9:20-9:30	Dedication: C.D. Keeling (Pieter Tans)

WMO/IAEA

9:30-9:50	**L. Barrie**	The WMO Global Atmosphere Watch (GAW) Programme in The Context Of Integrated Global Observations

Standards and Calibration (Chair: B. Hall)

9:50-10:10	**Y. Tohjima**	Preparation of gravimetric CO_2 standards by one-step dilution method
10:10-10:30	--**Break**--	
10:30-10:50	**P. Tans**	Revision of the international calibration scale for CO_2-in-air: WMO-X2005
10:50-11:10	**L. Zhou**	Round robin update
11:10-11:30	**S. Ishidoya**	Preparation of a large amount of standard air for O_2/N_2 measurements
11:30-11:50	**A. Jordan**	Calibration of Atmospheric HydrogenMeasurements
11:50-1:05	--**Lunch**--	

Handling of Calibration Gases (Chair: B. Hall)

1:05-1:25	**P. Sturm**	Thermal fractionation effects associated with Ar/N_2 measurements
1:25-1:45	**R. Keeling**	O_2/N_2 and Ar/N_2 measurements and fractionation issues
1:45-2:30	**Discussion Concerning Standards and Handling of Calibration Gases (P. Tans and R. Keeling)**	
2:30-2:50	--**Break**--	
2:50-3:30	**Recommendations concerning Standards and Handling of Calibration Gases**	
3:30-5:30	**Poster Session**	

Tuesday, September 20

Intercomparison Activities (Chair: M. Schmidt)

8:30-8:50	**N. Gavrilov**	Intercomparison of optical and in situ CO_2 measurement
8:50-9:10	**H. Mukai**	About disagreement between inter-comparisons of isotopic ratio measurements for CO_2
9:10-9:30	**I. Levin**	Results from the International Sausage Flask Intercomparison
9:30-9:50	**A. Manning**	GOLLUM: A Worldwide O_2/N_2 Intercomparison Programme - First Results
9:50-10:10	**D. Worthy**	Alert GAW Station: ICP - Programme Update and Possible Super Site?
10:10-10:40	--**Break and Group Photo--**	
10:40-11:30	**Discussion (A. Manning)** **Recommendations concerning Intercomparison Activities**	
11:30-12:50	--**Lunch--**	

Isotope Calibration and Measurement (Chair: D. Lowe)

12:50-1:10	**L. Huang**	A diagnostic tool for traceability difference/standard shifting in isotope measurements of atmospheric CO_2 & ICP at Alert
1:10-1:30	**W. Brand**	Relating air-CO_2 isotope ratio determinations to VPDB using Calcite-CO_2 mixed into CO_2-free air
1:30-1:50	**J. White**	INSTAAR/NOAA programme on isotopes in greenhouse gases
1:50-2:10	**D. Lowry**	Continuous automated carbon isotopic measurements of atmospheric methane or carbon dioxide using a modified GV Instruments Trace Gas pre-concentrator
2:10-2:30	--**Break--**	
2:30-2:50	**C.S. Wong**	Time-series air-sea disequilibrium of ^{13}C and CO_2 in subarctic Pacific and at arctic WMO station at Alert
2:50-3:10	**I. Levin**	Overview of recent ^{14}C measurements
3:10-3:30	**S. Lehman**	CMDL/INSTAAR ^{14}C measurement activities
3:30-5:00	**Discussion (W. Brand and J. Miller) Recommendations concerning Isotope Calibration and Measurements**	

Wednesday, September 21

CO_2 Measurements

1. Low-Cost, Robust CO_2 Measurement Systems (Chair: T. Machida)

8:30-8:50	**K. Davis**	Progress with continuous, flux-tower basedCO_2 sensors: Instrumentation and analyses

8:50-9:10	**M. Laakso**	A rugged NDIR CO_2 measurement probe for environmental studies
9:10-9:30	**M. Hahn**	The AOS Carbon Dioxide Archive: Vertical Profiles above Ameriflux (40.734N, 104.301W) in Northeastern Colorado
9:30-9:50	**B. Stephens**	An Autonomous, Inexpensive, and Robust CO_2 Analyzer (AIRCOA)
9:50-10:10	**--Break--**	

2. New CO_2 Measurement techniques (Chair: T. Machida)

10:10-10:30	**T. Machida**	New CO_2 Measurement Systems Using Aircraft
10:30-10:50	**J. Welles**	Assessing LI-COR's Factory CO_2 Calibration
10:50-11:50	**Discussion and Recommendations concerning in situ CO_2 Measurements (B. Stephens)**	
11:50-1:10	**--Lunch--**	

Data Management and Quality Assurance (Chair E. Brunke)

1:10-1:30	**Y. Tsutsumi**	Current Status and Advances of World Data Centre for Greenhouse Gases (WDCGG) Operation
1:30-1:50	**E. Scheel**	Quality Assurance and Quality Control for N_2O
1:50-2:10	**J. Klausen**	Quality Assurance and Quality Control of CO and CH_4 Measurements in GAW
2:10-2:30	**--Break--**	
2:30-3:00	**Discussion (E. Scheel)**	
3:00-3:30	**Recommendations concerning Data Management and Quality Assurance**	
3:30-5:00	**Recommendations concerning CH_4 (E. Dlugokencky); CO (P. Novelli); and N_2O (B. Hall)** **Discussion of any topics** **Draft of Recommendations (I. Levin)**	

Thursday, September 22

Regional Networks (L. Haszpra)

8:30-8:50	**P. Ciais**	Atmospheric CO_2 and greenhouse gases observations in the CarboEurope programme
8:50-9:10	**A. Vermeulen**	The CHIOTTO tall tower programme in Europe: first results
9:10-9:30	**M. Schmidt**	RAMCES: The French network of atmospheric greenhouse gas measurements

9:30-9:50	**F. Kashin**	Measurements of Greenhouse Gases Contents in the Air near the Ground, in the Atmospheric Boundary Layer and in the Atmospheric Column to Study Their Variability
9:50-10:10	**M. Leuenberger**	First online CO_2 and O_2 measurements at the Swiss high alpine research stationJungfraujoch
10:10-10:30	--**Break--**	
10:30-10:50	**A. Andrews**	The NOAA CMDL Tall Tower Trace Gas Observing Network
10:50-11:10	**C. Sweeney**	CMDL Aircraft Network Technical Progres Report
11:10-12:00	**Discussion Concerning Regional Networks (A. Andrews)**	
12:00-1:20	--**Lunch--**	
1:20-2:30	**Recommendations concerning Measurement Strategies** **Discussion of any topics**	
2:30-3:00	--**Break--**	
3:00-5:00(5:30)	**Discussion and Approval of Draft Recommendations (I. Levin)**	
5:00(5:30)	Meeting is adjourned	
6:30	**Cocktails-University Club at Folsom Field**	
7:00	**Banquet-University Club at Folsom Field**	

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WORKSHOP PROCEEDINGS

THIS WILL BE COMPLETED BEFORE GOING TO PRINT

Index by countries: the page #'s of reports in which country activities are mentioned.

Country	Report		
Australia	van der Schoot	Schmidt	
Brazil	Gatti		
Canada	Worthy	Schmidt	
China	Zhou		
Finland	Laurila		
France	Galdemard	Schmidt	Vermeulen
Germany	Vermeulen		
Greece	Schmidt		
Hungary	Haszpra	Vermeulen	Schmidt
India	Atri	Galdemard	Schmidt
Ireland	Vermeulen	Schmidt	
Italy	Santaguida	Vermeulen	
Kyrgyzstan	Gavrilov		
Netherlands	Vermeulen		
Poland	Vermeulen		
Russia	Gavrilov	Kashin	Schmidt
South Africa	Brunke	Schmidt	
Spain	Gomez-Pelaez	Vermeulen	Schmidt
Switzerland	Leuenberger		
UK	Fisher	Vermeulen	
USA	Gavrilov	Stephens	

Index by gases: the page #'s of reports in which gas activities are mentioned.

CO_2	CH_4	CO	N_2O	H_2	SF_6	Isotopic ratios	O_2	CO_2 flux	All gases
Gomez	Gomez	Laurila	Gomez*	Jordan	Gomez*	Schmidt	Ishidoya	Haszpra	Tsutsumi
Brunke	Brunke	Schmidt	Atri*		Laurila	Brand	Sturm	Laurila	Worthy
Zhou	Zhou	Klausen	Laurila		Schmidt	Mukai	Leuenberger		
Haszpra	Atri*	Kashin	Schmidt		Gatti	Fisher	Vermeulen		
Atri*	Laurila	Gatti	Scheel		Vermeulen	Vermeulen			
Laurila	Schmidt	Vermeulen	Gatti						
Santaguida	Klausen		Vermeulen						
Schmidt	Fisher								
Tans	Kashin								
Tohjima	Gatti								
Wong	Vermeulen								
Gavrilov									
Galdemard									
van der Schoot									
Stephens									
Leuenberger									
Fisher									
Kashin									
Gatti									
Vermeulen									

1. CALIBRATIONS AND STANDARDS

1.1 Revision of the International Calibration Scale for CO_2-in-Air: WMO-X2005

P. Tans[1], C. Zhao[2] and K.Thoning[1]
[1] *NOAA Earth System Research Laboratory, Global Monitoring Division*
[2] *Cooperative Institute for Research in Environmental Sciences, University of Colorado, Boulder*

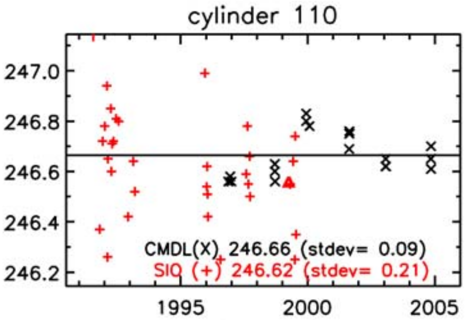
1.1.1 Manometric Measurements through 2005

The fifteen GMD Primary Standards that define the current WMO Mole Fraction Scale for CO_2-in-air have been in existence since early 1991. They became the Primary Standards of the WMO scale through a decision made by the participants during the WMO CO_2 Experts meeting in 1995. Initially in 1991 CMDL carried out a provisional calibration of the 15 cylinders relative to its then highest level scale, consisting of the "green cylinders", which had been calibrated multiple times by the Scripps Institution of Oceanography (SIO). The first direct calibration of the 15 cylinders was performed by SIO during 1991-1992, which was the WMO Central Calibration Laboratory (CCL) until 1995. Three additional calibration episodes by Scripps followed, in 1996, 1997, and 1999. All were done by infrared analyzer relative to the Scripps working standards, preferably during times when the Scripps working standards had just been recalibrated against the previous WMO Primary Standards which have remained at Scripps. In addition, in 1999, eight of the current fifteen WMO Primary Standards were calibrated once directly by the manometric system at Scripps. The manometric calibration system at Scripps has always been completely independent from the manometric system maintained by GMD.

GMD has until now carried out six manometric calibration episodes of the Primaries, in 1996, 1998, 2000, 2001, 2003, and 2004. The manometric system has been described by Zhao et al. (1997), and the description of its performance was updated by Zhao and Tans (2005). During each such calibration episode the CO_2 mole fraction in dry air of each Primary was determined three or more times. All calibration results of the Primaries are shown in Figure 1. The absolute uncertainty, defined as how far the CMDL calibrations may be removed from the true mole fraction, is estimated as 0.068 µmol/mol (one sigma) (Zhao and Tans, 2005). The repeatability (defined as the standard deviation of repeated individual measurements of each cylinder within each calibration episode) has improved over time from 0.12 µmol/mol to 0.04 µmol/mol (Table 1). The average of all cylinders during each episode varies between episodes with a standard deviation of 0.04 µmol/mol, which suggests small systematic variations of procedure, equipment, and/or measurement environment between episodes, but not a trend. The latter statistic comes closer to the concept of "reproducibility" as defined in the Recommendations section of this report.

Table 1: Comparison of GMD calibration episodes of WMO Primaries.

Measurement Episode	Number of measurements	Repeatability (one Std.Dev.) (ppm)	Average difference from WMO-X2005 (ppm)
1996	64	0.12	-0.06
1998	58	0.14	0.03
2000	55	0.11	0.06
2001	62	0.09	0.01
2003	62	0.06	-0.04
2004	48	0.04	-0.01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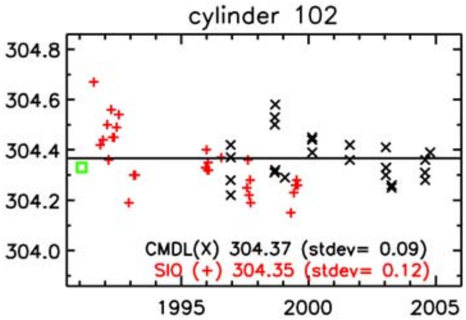
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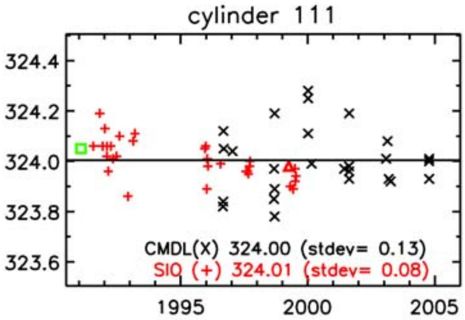
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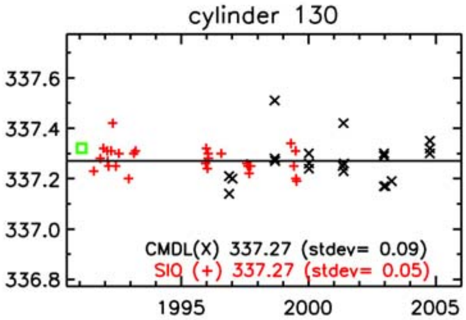
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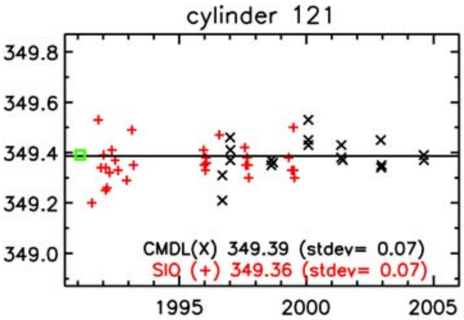
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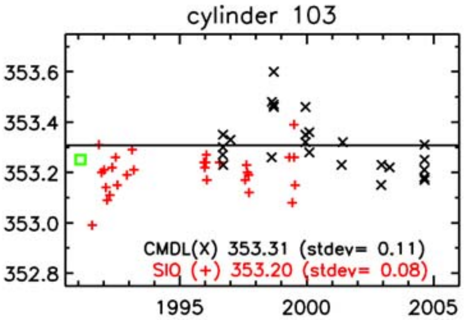
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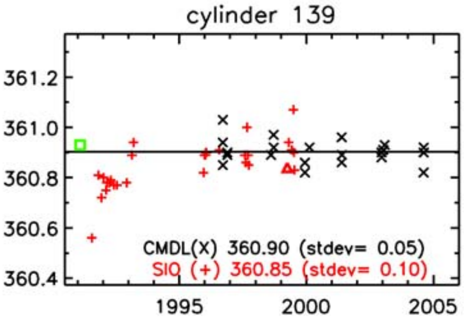
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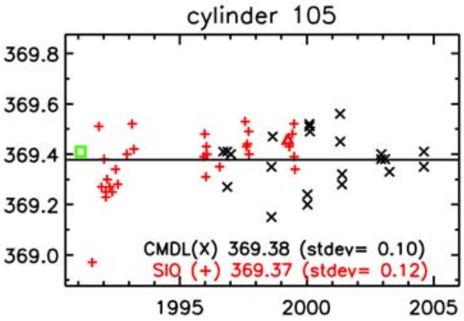
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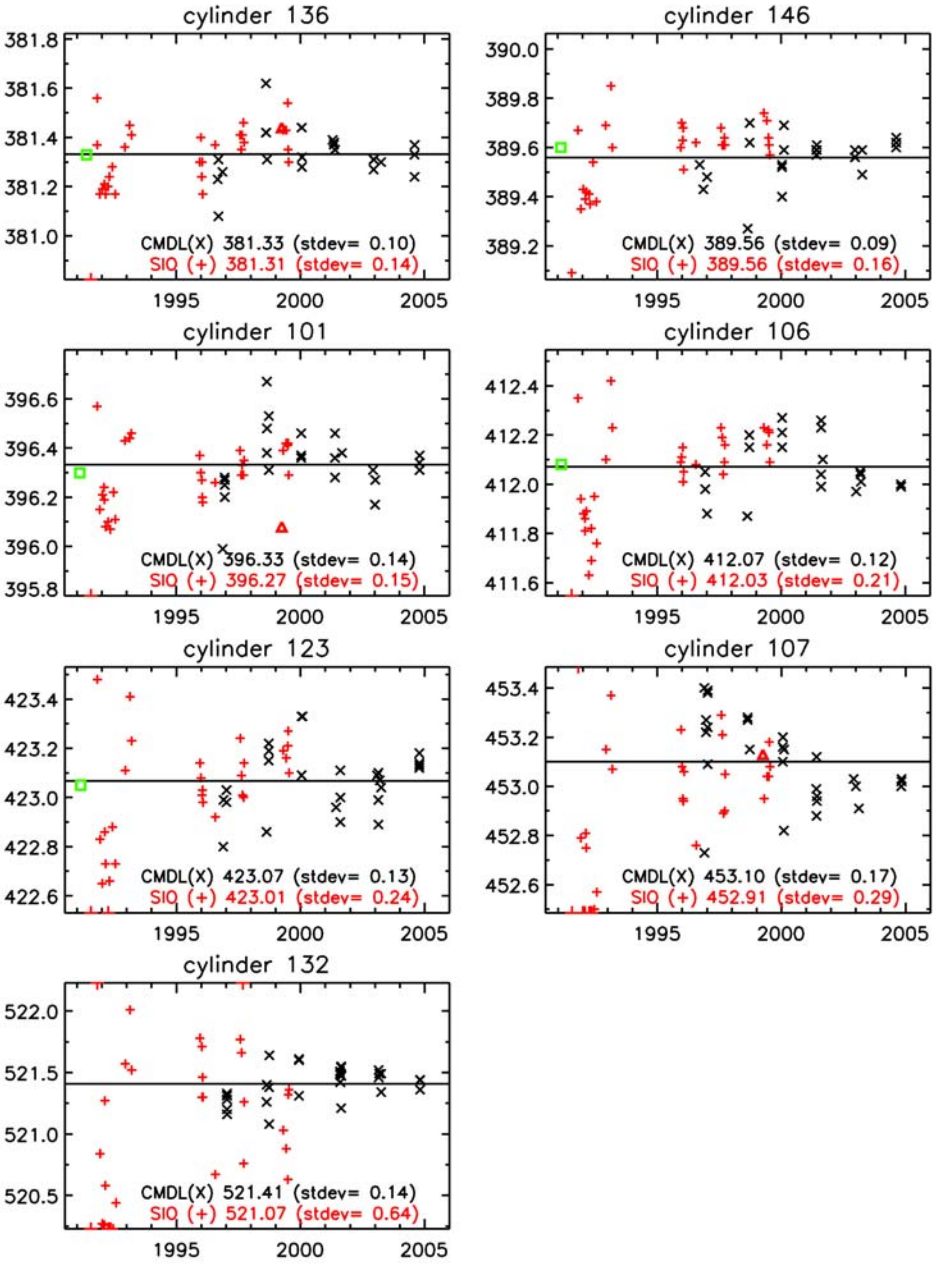

Figure 1: All calibrations performed on the WMO Primary reference gas mixtures of CO_2-in-air through 2005. Crosses, GMD manometric measurements; Red “plus” symbols, infrared measurements at the Scripps Institution of Oceanography (SIO) relative to the previous set of WMO Primaries maintained by David Keeling at SIO; Green squares, infrared measurements by CMDL based on the “green cylinders” traceable to the previous WMO Primaries at SIO; Triangles, direct manometric measurements by SIO. Values falling outside the plot ranges are depicted on the upper or lower axes. The averages and one-sigma standard deviations of individual measurements relative to each overall average are written on the plots. The vertical range of all plots equals 1 ppm except for the highest mole fraction at 521.4 ppm. The horizontal line is the average of all six GMD calibration episodes and represents the value currently assigned to the cylinder.

The null hypothesis, namely that there has been no drift of the mole fraction, cannot be rejected for the Primaries with the statistics we have. Therefore, we assume that there has been no drift so far, and the assigned value for each primary is the average obtained for that cylinder during all GMD calibration episodes. The only exception at this point is cylinder 107 at 453 ppm, which may be drifting downward, but we are still withholding judgement. Our procedure is illustrated in Figure 2. For each cylinder the average of each episode is plotted together with its uncertainty. The uncertainties are estimated by adding in quadrature (assuming independence) the standard deviation of the average of all cylinders during each episode (column 4 in Table 1), 0.044 ppm, and the repeatability of individual cylinder determinations in each episode (column 3 in Table 1, divided by the square root of the number of measurements of each cylinder during that episode). The uncertainties (one sigma) typically decrease from 0.075 ppm in 1996 to 0.05 ppm in 2004. In the case of cylinder 146, there is a probability of ~0.70 that the reduced chi-square value (X_v) will be larger than 0.59 (5 degrees of freedom). In other words, our null hypothesis of zero drift cannot be rejected. For cylinder 101, the probability of exceeding 2.36 (Figure 2) is ~0.035. The hypothesis of a constant value is therefore not all that good, but the hypothesis of linear drift is no better!

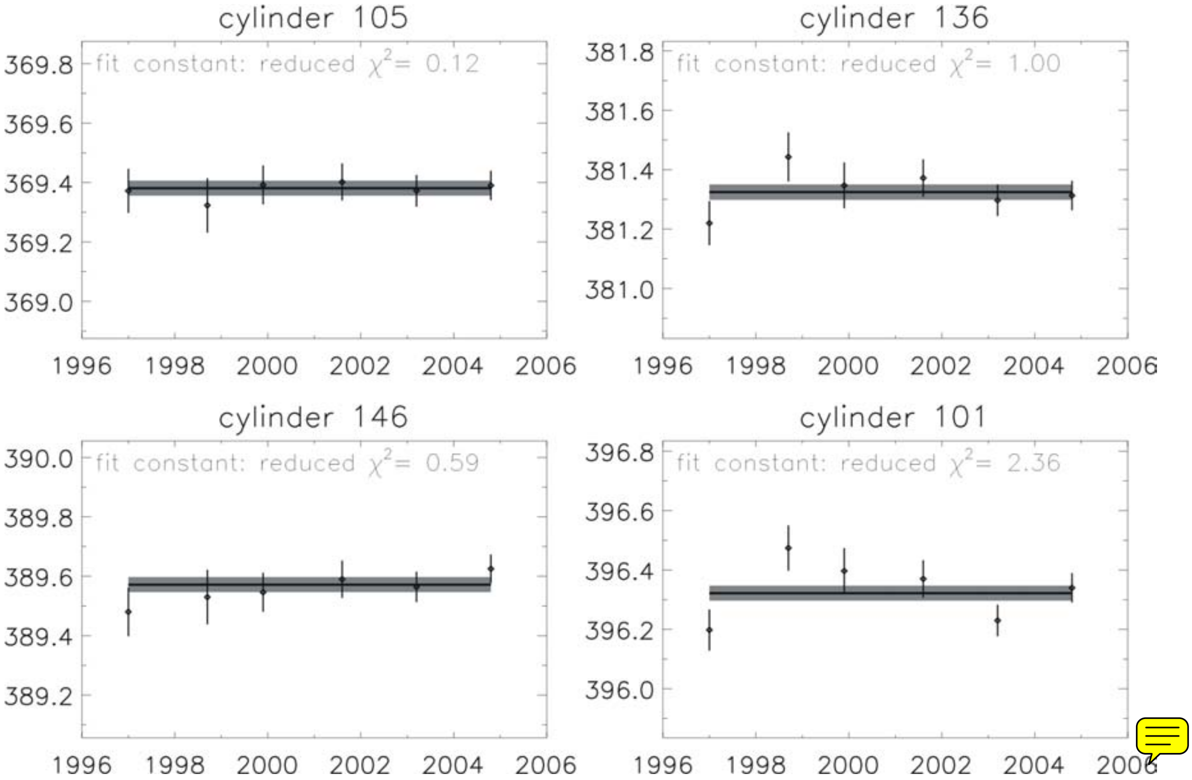

Figure 2: **The average measured value for each episode with its estimated uncertainty. The horizontal line is the mean of all episodes, weighted by their uncertainties, while the shaded area represents the one sigma uncertainty of the mean.**

1.1.2 Revisions of Earlier Calibrations Performed by GMD to the WMO-X2005 Scale

The analysis above does not imply that the WMO Scale as defined in the past has not drifted. This is mainly due to revisions of the calibrations performed by Scripps between 1991 and 1999. The early assigned values of the Primaries were based entirely on the infrared calibrations by Scripps. From 1996 through the fall of 2001 they were determined both by Scripps and GMD calibrations. After the latter date the assigned values were determined exclusively by GMD (manometric) calibrations. The average of all assigned values to the Primaries increased by 0.14 µmol/mol from 1996 to 2005. From late 2001 until 2005 the average of all assigned values of the Primaries has decreased by 0.01 µmol/mol.

In June 2002 GMD received revised numbers from SIO for their four calibrations of the fifteen WMO Primaries that were carried out from 1991 to 1999 (Guenther et al., 2002). Scripps experienced some apparent inconsistencies between the mole fractions of their Primaries and their manometer. Their revised scale was called X99A, which assumed constancy of their Primary references gases, implying some variations of the ratio of the small volume to the large volume of their manometric apparatus. This choice provided very good consistency with the GMD calibrations. The average of all Scripps calibrations of all of our Primaries on the X99A scale was 0.06 µmol/mol higher than the average of all CMDL calibrations, while their average in the ambient range (345-415) was 0.02 µmol/mol higher than ours. Scripps also provided us with values for our 15 Primaries based on their X99B scale, which assumed that their manometric volume ratio had remained constant, implying that the Scripps Primaries displayed some drift. This alternative choice would imply that most of our Primaries have drifted considerably between 1991 to 1999, from zero at the low end of the scale to about 0.1 ppm/year at 520 ppm, and that the averages of the Scripps calibrations are higher than GMD's, varying from about 0.1 to 0.3 ppm. Currently, we are disregarding the X99B scale as too inconsistent with GMD calibrations of the 15 cylinders. However, the discrepancy is still under active investigation, and more evidence from comparisons with other methods at Scripps can be brought to bear on the issue.

In addition, in 2005 we carried out, at the request of Y. Tohjima of the National Institute of Environmental Studies (NIES), infrared calibrations of five new gravimetric standards (approx. 350 and 390 micromol/mol) made by one-step dilution by Japan Fine Products Company. The average of the NIES values was lower than GMD's by 0.004 µmol/mol, and the standard deviation of the individual comparisons was 0.02 µmol/mol.

Figure 3 shows the actual mole fraction assignments of the fifteen Primaries as they have been from 1991 until 2005. They clearly have drifted over time, particularly at the high end of the range. Once again, the curves are based (mostly) on the original values received from SIO, and do not correspond to the revised values based on the SIO X99A scale that have been plotted in Figure 1.

Based on the assumption that the fifteen Primaries have been stable, we have re-assigned a constant value (the average of the measured values during the six CMDL calibration episodes) to each of them all the way back to 1991. Also the GMD "Green Cylinders" received new values based on the Scripps X99A scale, and they are now in good agreement with the revised values for the fifteen Primaries (see Figure 1). We call this revised scale WMO-X2005, and we have applied it to GMD calibrations going back to 1979.

The calibration scale has always been first transferred to "secondary" reference gas mixtures at GMD using an NDIR analyzer. This is done to lengthen the life of the Primaries, so that a long calibration history can be established for each of them. The Secondaries have in turn been used to calibrate all other cylinders. The calibrations of the Secondaries, and subsequently of all other CO_2 reference gas cylinders, have been recalculated using the new WMO-X2005 scale. The revisions, more than 9500, are summarized in Figure 4 as a function of time and as a function of mole fraction. All laboratories and individuals for whom we have calibrated CO_2 standards in the past will be able to read the revised values of their reference gases from the GMD website (www.cmdl.noaa.gov/ccgg/refgases/) by clicking on "CMDL Calibration Results for Standard Reference Gases" and entering the cylinder number of their reference gases, or they may contact Mr. Duane Kitzis at GMD (Duane.R.Kitzis@noaa.gov). After we had made the change in scale and compared the old and the new assigned values to cylinders there were a number of discrepancies that were clearly too large. They were due in large part to missing code in the data base for some cylinder refills and notes about problems that occurred during particular transfer calibrations that were also not recorded in the data base. We believe that we have (as of April 2006) found most of the errors, but encourage users to contact Duane Kitzis if they believe there is an error in the new calibration value for a cylinder.

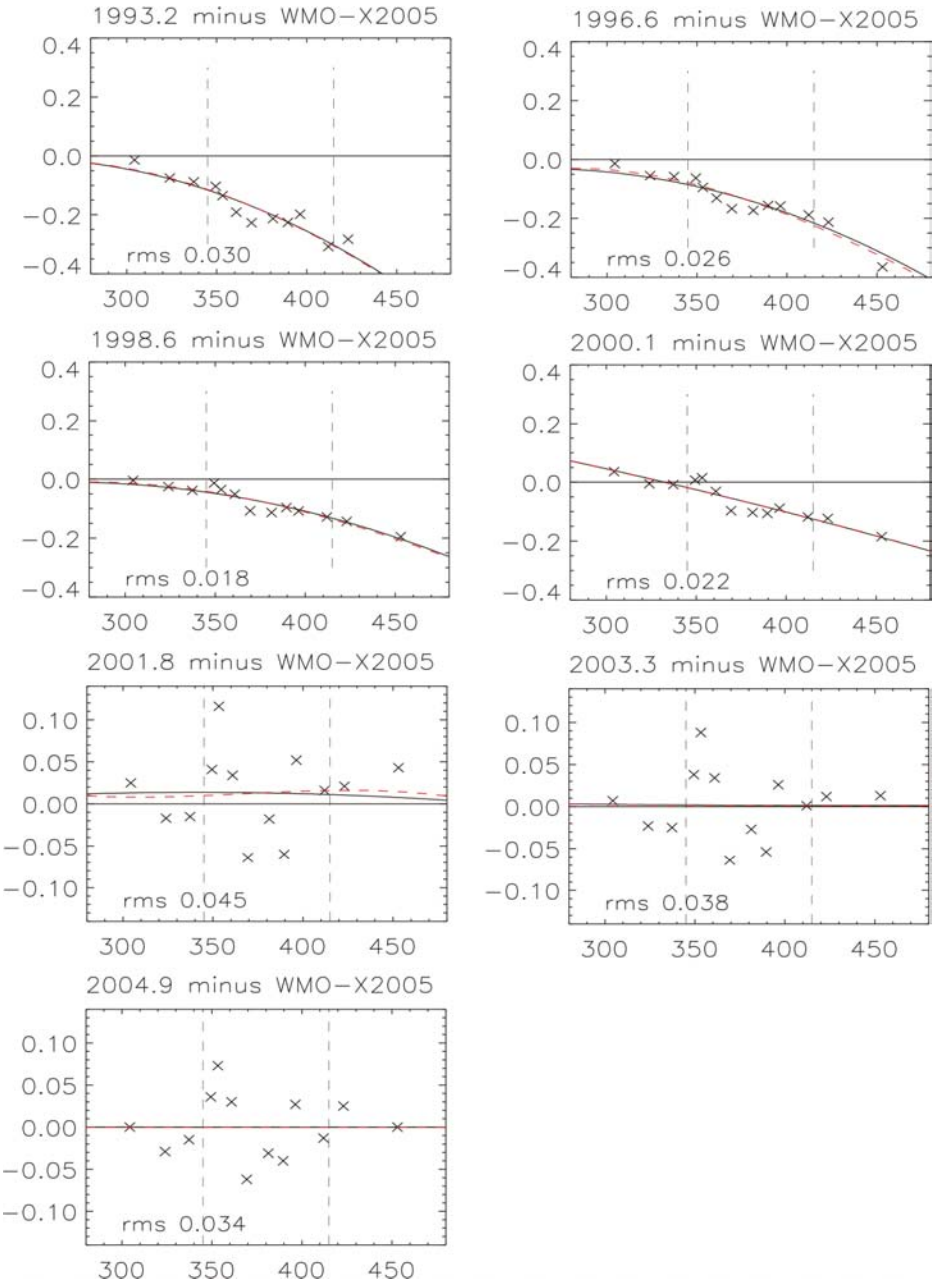

Figure 3: History of mole fraction assignments, plotted as deviations from the WMO-X2005 scale, of the fifteen WMO Primary reference gases. Note the change in vertical scale between 2000.1 and 2001.8. The rms values (bottom left on each graph) are with respect to the smooth curves (solid line, quadratic; dashed line, cubic) fitted to the differences between the old assignments and WMO-X2005. The assignments based (mostly) on the infrared calibrations show less scatter, but also a substantial systematic mole fraction-dependent difference from WMO-X2005. Since the WMO-X2005 scale is defined as the quadratic curve fit to the IR analyzer voltage response to the assigned values in the range 300-460 ppm in 2004.6, the scatter around zero of 0.034 ppm in the last plot represents the scatter to that curve fit.

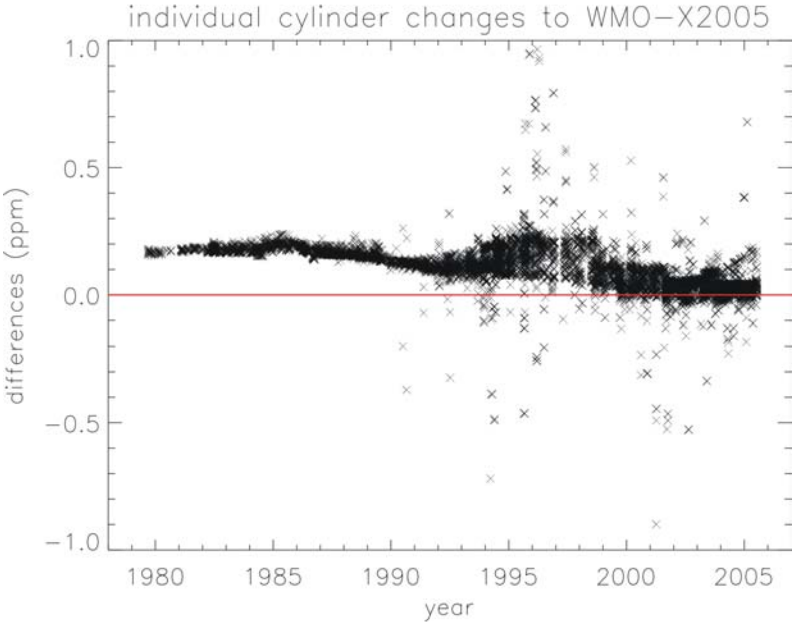

Figure 4a: Revisions to all CO_2 calibrations by GMD as a function of time. The smaller scatter during the 1980s is due to the very narrow mol fraction range of ambient CO_2 in background air that was being calibrated.

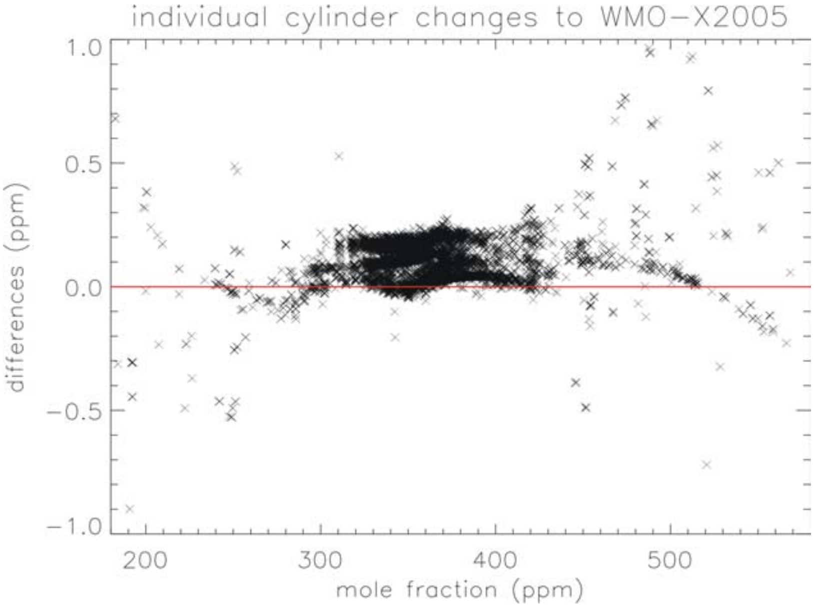

Figure 4b: Revisions to all CO_2 calibrations by GMD as a function of mole fraction. The figure illustrates that the revisions can be very substantial for cylinders outside of the range 300-430 ppm.

References

Guenther, P.R., A. Bollenbacher, C.D. Keeling, and D. Moss, Technical Report: Infrared Analyses of NOAA Primary CO_2-in-Air Reference Gas Standards at SIO, 1991-1999, Scripps Institution of Oceanography, March 2002.

*Zhao, C., P.P. Tans, and K.W. Thoning, A high precision manometric system for absolute calibrations of CO_2 in dry air, **J. Geophys. Res. 102,** 5885-5894, 1997.*

*Zhao, C., and P.P. Tans, Estimating uncertainty of the WMO Mole Fraction Scale for carbon dioxide in air, **J. Geophys. Res. 110**, doi: 10.1029/2005JD006003R, 2005.*

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1.2 Preparation of Gravimetric CO_2 Standards by One-Step Dilution Method

Y. Tohjima[1], T. Machida[1] and H. Mukai[1], M. Maruyama[2], T. Nishino[2], I. Akama[3], T. Amari[3] and T. Watai[4]

[1] *National Institute for Environmental Studies*
[2] *Chemicals Evaluation and Research Institute*
[3] *Japan Fine Products Corp., Kawasaki*
[4] *Global Environmental Forum, Tsukuba*

Abstract

We have developed a technique to prepare gravimetric CO_2-in-air standard gases with atmospheric levels of CO_2 concentration in 10-L aluminium cylinders using a one-step dilution. The masses of the purified CO_2 (about 0.7 g) and the diluent air (CO_2 free air, about 1.2 kg) are determined by precise analytical balances with appropriate precisions. Chemicals Evaluation and Research Institute (CERI) and Japan Fine Products Corp. (JFP) have prepared 15 CO_2 standards each. CERI and JFP use their individual precise balances and gas-handling lines. The CO_2 mole fractions have been measured by a nondispersive infrared (NDIR) analyzer against the NIES (National Institute for Environmental Studies) CO_2 standard scale. The averages and standard deviations (1σ) of the differences between the gravimetric and NDIR values (gravimetric – NDIR) are –0.004 ± 0.125 $\mu mol\ mol^{-1}$ for CERI and 0.076 ± 0.042 $\mu mol\ mol^{-1}$ for JFP.

1.2.1 Introduction

At the present time, one of the reliable methods for providing an accurate standard scale for the atmospheric CO_2 mole fraction is the manometric method. In this method, the temperatures, pressures and volumes of the air and the extracted CO_2 are precisely measured and the CO_2 mole fraction is determined by solving the equations of state for the air and CO_2 gases. *Zhao et al.* [1997] developed a high-precision manometric system to calibrate CO_2 mole fraction and estimated the uncertainty to be about 0.06 $\mu mol\ mol^{-1}$ (ppm).

In addition, the gravimetric method can also provide accurate CO_2 standards. In Japan, Tohoku University, jointly with Nippon Sanso Corp., developed a gravimetric dilution method to prepare CO_2-in-air standard gases. The standard gases with ambient levels of CO_2 were first prepared in a two-step dilution [*Tanaka et al.*, 1983], but later the number of the dilution steps was increased to three [*Tanaka et al.*, 1987]. The precision for the three-step dilution was estimated to be 0.13 $\mu mol\ mol^{-1}$ [*Tanaka et al.*, 1987] (see Figure 1).

The National Institute for Environmental Studies (NIES) purchased a set of 8 gravimetric CO_2 standards prepared by Nippon Sanso Corp. in 1995 using the 3-step dilution method. The NIES CO_2 standard scale is based on these 8 gravimetric standards. After 1995, NIES purchased other sets of gravimetric CO_2 standards from Nippon Sanso Corp. and Taiyo Toyo Sanso Corp. However, these CO_2 standard scales based on the individual sets of gravimetric standards show larger differences relative to each other than the expected uncertainty (Figure 1). It is noteworthy that Nippon Sanso Corp. and Taiyo Toyo Sanso Corp. were merged into Taiyo Nippon Sanso Corp. in 2004 and that JFP is a wholly owned subsidiary of Taiyo Nippon Sanso Corp.

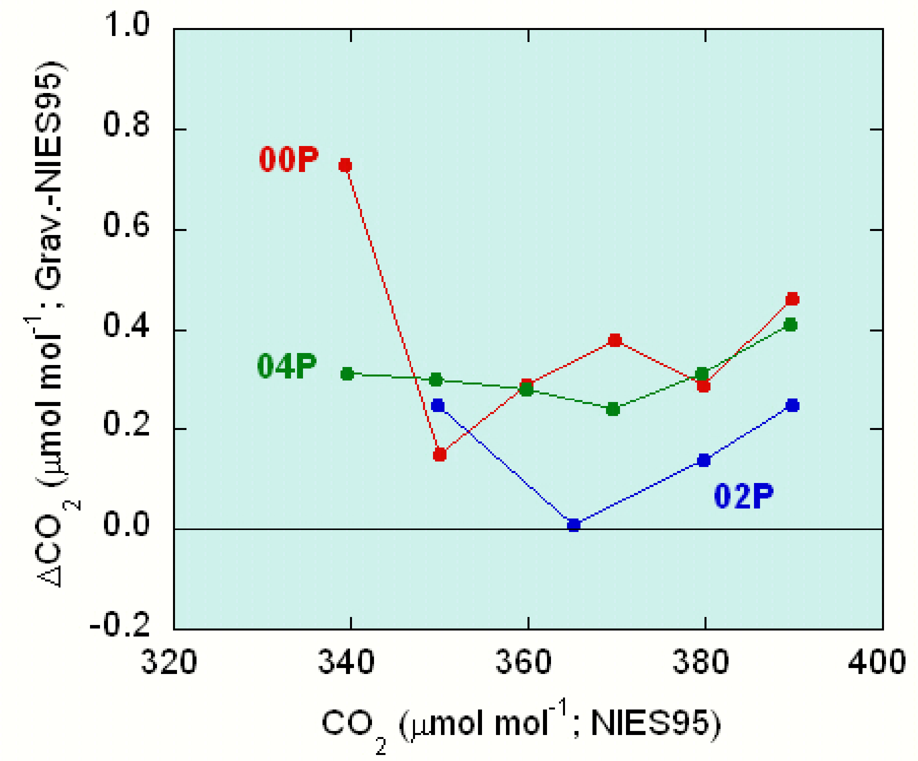

Figure 1: **Comparison of the gravimetric CO_2 mole fractions prepared using a three-step dilution method. Differences in the CO_2 mole fraction relative to the NIES-95 scale, which is also based on a set of 8 gravimetric standards prepared in 3-step dilution, are plotted. Each colour represents a set of granddaughter standards derived from the same daughter standard.**

In the three-step dilution method, there is a hierarchy of three levels of standards: parent (high level of CO_2), daughter (middle level), and granddaughter (ambient level). One daughter can produce about 8 granddaughters. The above mentioned set of gravimetric CO_2 standards was a series of granddaughters derived from one daughter standard. Therefore, the internal precision of each set of CO_2 standards is fairly good because relative differences of the CO_2 mole fraction are only affected by the errors associated with the final dilution processes. The differences in the CO_2 scales relative to each other may be ascribed to the fact that the standards were derived from the different daughter or parent. Although the uncertainty in the three-step dilution should be evaluated from the independent CO_2 standards, large numbers of parents and daughters are wasted if lots of independent granddaughters are prepared in the three-step dilution.

The one-step dilution method has two advantages: (1) reduction of dilution steps may reduce the uncertainty associated with mass determination and gas handling processes, and (2) each standard is independent of other standards. In the following, we describe the gravimetric one-step dilution method for preparing CO_2 standard gases and evaluate the reproducibility.

1.2.2 Preparation of Gravimetric Standard in 1-Step Dilution

1.2.2.1 Principle

Pure CO_2 gas is transferred from a small flask into a 10L cylinder, and then the cylinder is filled with diluent gas. The masses of the pure CO_2 gas and the diluent air in the standard gas are determined accurately, and the mass mixing ratio is converted to a mole fraction. The CO_2 flask is weighed on a highly precise electronic balance and the 10L cylinder is weighed on a large balance (a pair of scales). The masses of the CO_2 gas and diluent gas are calculated from the changes in the mass of the CO_2 flask and the 10L cylinder, respectively.

In this study, the gravimetric CO_2 standards with the mole fractions ranging from 350 to 390 µmol mol^{-1} were prepared at CERI and JFP, where different balances and gas manifolds are used. Since the final pressures of the gravimetric standards are usually about 10 MPa, the cylinders were filled with the pure CO_2 gas of 0.6 ~ 0.7 g and the diluent gas of 1.2 kg.

1.2.2.2 Cylinders and source gases

The CO_2 gravimetric standards were prepared in 10-L aluminium cylinders (Luxfer, Riverside, CA) fitted with brass, diaphragm valves with taper threads (Hamai Co. Ltd., Japan). Before use of the cylinder, we treated its inner surface as follows. First, we polish the inner surface to a mirror like finish (surface roughness of about 1µm) by rotating the cylinder with abrasive in it. After the inner surface is washed with pure water, the diaphragm valve is attached to the cylinder. Then the cylinder is filled with O_2 and is heated to inactivate the inner surface.

We used highly-purified CO_2 gas (G1-grade, JFP) as source gas for the standards. As the diluent gas we used clean-up air (G1-grade, JFP) because the other gases, such as pure nitrogen gas, may affect the CO_2 response of NDIR analyzer [*Griffith* et al., 1982]. The impurities in the CO_2 gas and the clean-up air, the isotopic compositions of the CO_2 gas, and the major composition of the clean-up air are discussed in Section 3.2 and 3.3.

1.2.2.3 Preparation Procedure

A small stainless steel flask (internal volumes of about 250 cm^3 for CERI and 100 cm^3 for JFP) with a valve is connected to the gas manifold (Figure 2) and evacuated to about 0.1 Pa. Then the flask is filled with the pure CO_2 gas to the pressure, which gives the target concentration of the gravimetric standard when the CO_2 gas is expanded to the 10-L cylinder as is described later. The CO_2-filled flask is weighed on a precise electronic balance (Mettler-Toledo, model AX205 for JFP and Mettler-Toledo, model AT 1005 for CERI). Similarly, the 10-L cylinder is evacuated to about 0.1 Pa and is weighed by a precise balance with a capacity of 30kg and a nominal precision of 1 mg.

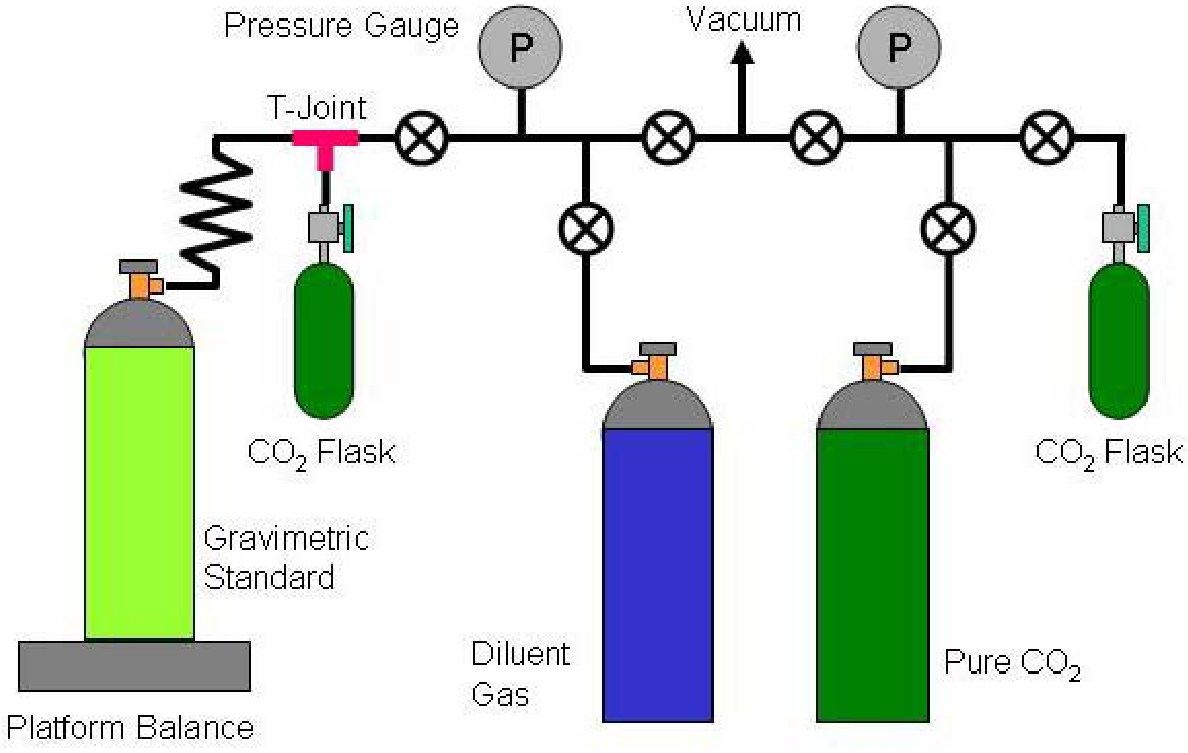

Figure 2: **Schematic of the gas manifold used in the preparation of the gravimetric standards.**

The evacuated cylinder, which is set on a platform balance with a nominal precision of 0.1 g, and the CO_2-filled flask are connected to the gas manifold via a T-joint (Figure 2). The lines of the manifold are evacuated to remove the room air, and the valve placed upstream of the T-joint is closed. Then the valves of the flask and the cylinder are opened to disperse the CO_2 gas throughout the lines of the manifold and the cylinder, and again the valves are closed. To transfer the CO_2 in the lines of the manifold to the cylinder, the lines are filled with the diluent gas to a pressure of about 1 MPa, and the valve of the cylinder is quickly opened and closed. This procedure is repeated more than 10 times to completely transfer the CO_2 gas in the line to the cylinder. After that, the flask and the T-joint are disconnected from the gas manifold. Again, the cylinder is directly attached to the gas manifold and the lines are evacuated. Finally, the diluent gas is transferred to the cylinder until the cylinder mass reaches the target mass, which gives the target concentration of CO_2.

The CO_2-filled flask is again weighed by the electronic balance. The 10-L cylinder, disconnected from the gas manifold, is also weighed by the precise balance. Note that the cylinder temperature is greater than the room temperature because of adiabatic compression just after the cylinder is filled with the diluent gas. Thus the cylinder is weighed at least 2 hours after gas filling procedure to allow equilibration of the cylinder temperature with the room temperature. The amount of CO_2 in the cylinder is calculated from the decrease in the mass of the flask. The increase in the mass of the cylinder corresponds to the sum of the masses of the CO_2 and the diluent gas.

The weighing procedure for the 10-L cylinder is the same as that described in *Tohjima et al.* [2005]. When the cylinder is weighed by the precise balance, another 10-L aluminium cylinder is placed on a pan on the opposite side of the beam to equalize the buoyant forces on both side of the beam. We use one more 10-L aluminium cylinder as the tare cylinder, alternately weigh the tare cylinder and the cylinder for the standard several times in a sequence of tare-standard-tare-...-tare, and determine the mass of the cylinder relative to the tare cylinder. Note that loading and unloading of the cylinders are automated. The small flask is also weighted relative to another identical flask (tare flask).

1.2.3 Calculation Of CO_2 Mole Fraction

The mole fraction of the standard is calculated as the number of moles of CO_2 divided by the total number of moles of the mixture of CO_2 and diluent gas. To obtain the correct mole fractions, we need to accurately evaluate the masses and the molecular masses of the CO_2 gas and the diluent gas. In the followings, we discuss the error sources in the determination of the mole fractions.

1.2.3.1 Buoyancy variations

Although we make several efforts to minimize the buoyancy effects, the changes in the buoyant force on the precise balances may still cause errors in the determination of the mass of the cylinder and flask. Here we evaluate the effect of the buoyancy changes caused by the change in volume of the cylinder and the change in the air density.

The volume of the 10-L aluminium cylinder increases almost linearly with internal pressure at an average rate of 22 ± 4 cm^3 per 10 MPa [*Tohjima et al.*, 2005], which corresponds to an increase in buoyancy of about 26 ± 5 mg. Therefore, the expansion of the 10-L cylinder results in the underestimate of the mass of the diluent gas. In our study, the buoyancy effects cause changes in the gravimetric mole fraction of 0.008 ± 0.002 $\mu mol\ mol^{-1}$. The mole fractions are corrected for this buoyancy effect.

The masses of the gases determined by the balances are not absolutely correct because of the buoyant forces on the weights, which are made of stainless steel with density of 7950 kg m^{-3}. If the air density is constant during the CO_2 standard preparation process, the buoyancy associated with the weights, being proportional to the mass of the weights, does not make errors in the calculations of the mole fraction. Although the laboratory was air-conditioned, the density of the ambient air must have changed during the preparation procedure. Unfortunately, we did not monitor these air conditions. Thus, we evaluate the range of the density for the change in the temperature of 25 ± 2 °C, pressure of 1013 ± 5 hPa, and relative humidity of ± 20%. The actual changes of the ambient condition are considered within the above range. The evaluated variation in the air density ranges from 1.17×10^{-3} g cm^{-3} to 1.20×10^{-3} g cm^{-3}, producing the errors of ± 2.5 mg for the diluent gas and about ± 1.5 µg for the CO_2. These errors correspond to the uncertainty in the CO_2 mole fraction of about 0.001 µmol mol^{-1} at most. Therefore, we conclude the effect of the buoyancy change associated with the variations in the air density is negligible.

1.2.3.2 Impurities in the source gases

We measured O_2, N_2, CO, CH_4, and H_2O in the pure CO_2 gas (Table 1). The results show that the concentrations of these impurities except H_2O are less than the detection limits but the concentration of H_2O is about 3.5 µmol mol^{-1}. Therefore, we believe that the sum of the impurities in the CO_2 gas is less than 4 µmol mol^{-1}, which reduces the CO_2 mole fraction of the standards by 0.002 µmol mol^{-1} at most. On the other hand, the CO_2 concentration in the diluent gas is below the detection limit of 0.01 µmol mol^{-1} (Table 2). Consequently, the effect of the impurity seems not to exceed 0.01 µmol mol^{-1}.

Table 1: **Impurities in the Source CO_2 Gas.**

Impurity	Detection limit (µmol mol^{-1})	Analyzed value (µmol mol^{-1})
O_2	0.1	ND
N_2	0.1	ND
CO	0.1	ND
CH_4	0.02	ND
H_2O	1	3.5

Table 2: **Impurities in the Diluent Gas.**

Impurity	Detection limit (µmol mol^{-1})	Analyzed value (µmol mol^{-1})
CO	0.1	ND
CO_2	0.01	ND
CH_4	0.01	ND
H_2O	1	ND

1.2.3.3 Molecular masses of CO_2 and diluent gas

Because the origin of the source CO_2 gas is burned petroleum, the stable isotopic ratios (δ^{13}C=-32‰ (VPDB) and δ^{18}O=0.0‰ (VSMOW)) are different from those of the atmospheric CO_2. Taking account of the isotopic ratios of VPDB and VSMOW, we obtain the mean CO_2 molecular mass of 44.0094 ± 0.0001.

The diluent gas is cleaned-up natural air (see Table 2). Thus, there is a possibility that the ratios of N_2:O_2:Ar are different from those for the ambient air because the purifying processes including the oxidation on Pt catalyst and trapping of CO_2 and H_2O on a Molecular Sieve 5A column could alter the ratios. To evaluate the composition of the diluent gas, we have measured the O_2, N_2, and Ar concentrations for each CO_2 gravimetric standard by GC/TCD method [*Tohjima et al.*, 2005], and found that the relative abundance of O_2 and Ar with respect to N_2 for the diluent gas is less than those for ambient air. The molecular masses of the diluent gases (CO_2 free) range from 28.9562 to 28.9579. The uncertainty of the molecular mass is evaluated to be 0.0002, which correspond to the error of the CO_2 mole fraction of about ± 0.003 µmol mol^{-1}.

1.2.3.4 Estimates of Uncertainties in Gravimetric CO_2 mole fraction

There are uncertainties associated with measurements of mass, of purity and molecular mass of source gases, and of buoyancy change caused by the expansion of cylinder and the change in the air density. Table 3 summarizes the sources of errors and estimates of the uncertainties in the mole fractions and ratios for the gravimetric standards. The overall uncertainties are 0.03 μmol mol^{-1}. The largest source of error is the uncertainty associated with the mass determination by the electric balance.

Table 3: Estimates of Uncertainty.

Source of error	**Uncertainty**[a]	**ΔCO_2**[a] **(μmol mol^{-1})**
Measurement of mass of CO_2	±50μg (±40μg)	±0.030 (±0.023)
Measurement of mass of diluent gas	±2.5mg (±3mg)	±0.0009 (±0.001)
Molecular mass of CO_2	±0.0001	±0.0009
Molecular mass of diluent gas	±0.0002	±0.003
Impurity of CO_2	<0.0004%	-0.002~0
CO_2 in diluent gas	<0.01 μmol mol^{-1}	<0.01
Air density change	$\pm 1.6\times10^{-5}$ g/cm^{3}[b]	±0.001
Expansion of cylinder	±5 mg	±0.002
Root Mean Square		±0.032 (±0.025)

[a] *Values in parentheses are uncertainties for CERI.*

[b] *The uncertainty is calculated for the conditions of T=25±2°C, P=1013±5hPa, and ΔHr=±20%.*

1.2.4 Results

Table 4 summarizes the gravimetric CO_2 mole fractions for the 30 standards prepared by CERI and JFP. For comparison, the CO_2 mole fractions measured by a nondispersive infrared (NDIR) analyzer (Shimadzu, Kyoto, model URA-207) against the NIES CO_2 scale based on the 8 primary standards are also shown. The differences in the CO_2 mole fraction between the gravimetric and analyzed values (gravimetric - analyzed value) are also listed in Table 4, and are plotted against individual mole fractions in Figure 3. The averages and the standard deviations of the differences are –0.004 ± 0.125μmol mol^{-1} for CERI (N=15) and 0.076 ± 0.042μmol mol^{-1} for JFP (N=15). Although the uncertainty of the gravimetric CO_2 mole fraction prepared by JFP is almost comparable to the estimated uncertainty, the uncertainty by CERI is more than 4 times larger than the estimated uncertainty. To investigate the source of the error, we carefully examined the preparation procedure at CERI, but we have not found the particular source. However, these results suggest that the 1-step dilution method is capable of calibrating CO_2 reference scale to an uncertainty of about ± 0.1 μmol mol^{-1}.

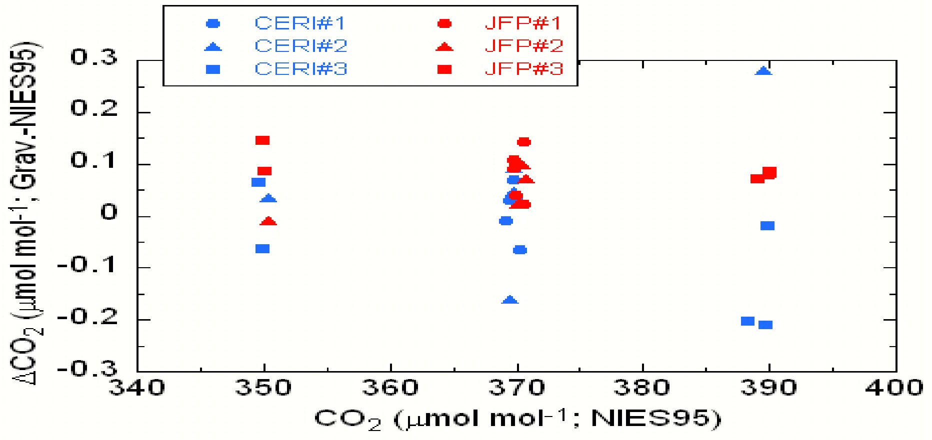

Figure 3: Differences in CO_2 mole fraction between the gravimetric value and the analyzed value by NDIR against the NIES-95 scale for standards prepared using the one-step method.

Table 4: List of CO_2 Gravimetric Standards[a].

CERI **Cylinder**	**Grav.**	**Grav.-NDIR**	**JFP** **Cylinder**	**Grav.**	**Grav.-NDIR**
CERI#1(2004/3/1~3/3)			JFP#1(2004/2/26~2/27)		
30510	370.14	-0.065	30089	369.88	0.110
30498	369.12	-0.008	30091	369.83	0.093
30497	369.44	0.031	30092	370.61	0.144
30514	369.91	0.034	30093	370.49	0.024
30492	369.79	0.070	30094	369.99	0.040
CERI#2(2004/7/15~7/21)			JFP#2(2004/7/15~7/17)		
30492	350.36	0.035	30089	350.27	-0.009
30497	369.37	-0.160	30091	370.46	0.100
30498	369.85	0.048	30092	370.08	0.024
30510	369.81	0.091	30093	370.66	0.073
30514	389.80	0.281	30094	389.73	0.079
CERI#3(2004/12/14~12/17)			JFP#3(2005/1/15~1/27)		
30492	349.85	-0.061	30089	350.14	0.086
30497	349.64	0.066	30091	350.02	0.145
30498	389.78	-0.017	30092	390.11	0.082
30510	389.70	-0.209	30093	390.11	0.088
30514	387.99	-0.203	30094	389.03	0.073
Ave. ±1σ		-0.004±0.125	Ave. ±1σ		0.076±0.042

[a] *Values are given in μmol mol^{-1}.*

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1.3 CO_2 Calibration Facilities at Climate Chemistry Laboratory in the Institute of Ocean Sciences of Fisheries and Oceans Canada

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1.3.1 Gases

1.3.1.1 Introduction

This report describes the CO_2 calibration facilities at the Climate Chemistry Laboratory in the Institute of Ocean Sciences of the federal Department of Fisheries and Oceans, Canada. The facilities were set up through funding from the PERD (Panel of Energy Research and Development) Programme in 1983. There are two facilities at the Laboratory: (1) gravimetric and (2) manometric. A post-doctoral fellow was hired for two years to work on both facilities.

The gravimetric facilities (Figure 1) consist of a gas transfer and mixing system, connected to a high vacuum, and high-accuracy weighing balances (Voland™ Jupiter 5000 balance capable of weighing 10 kg to 1 mg, or 10^{-7} and a Voland™ HCE 100G capable of 100 kg to 1 g).

Figure 1: **Gavimetric facilities showing the Voland™ Jupiter 5000 balance (left), and Voland™ HCE 100G balance (middle), and the gas transfer system (right).**

The manometric facilities (Figure 2) consist of a Caltech cathetometer capable of measuring a mercury height readable to ±0.002 mm mercury and accurate to ±0.005 mm mercury. The manometric chambers are comprised of a small chamber and large chamber of mercury. The mercury column is housed in a cabinet with temperature controlled to ±0.02ºC. In practice, the system is precise to 0.02%, or 1 part in 5,000. We tried a Ruska quartz-fibre manometer but did not use it for the inter-calibration since, although it gives fast results, it had a less stable reading.

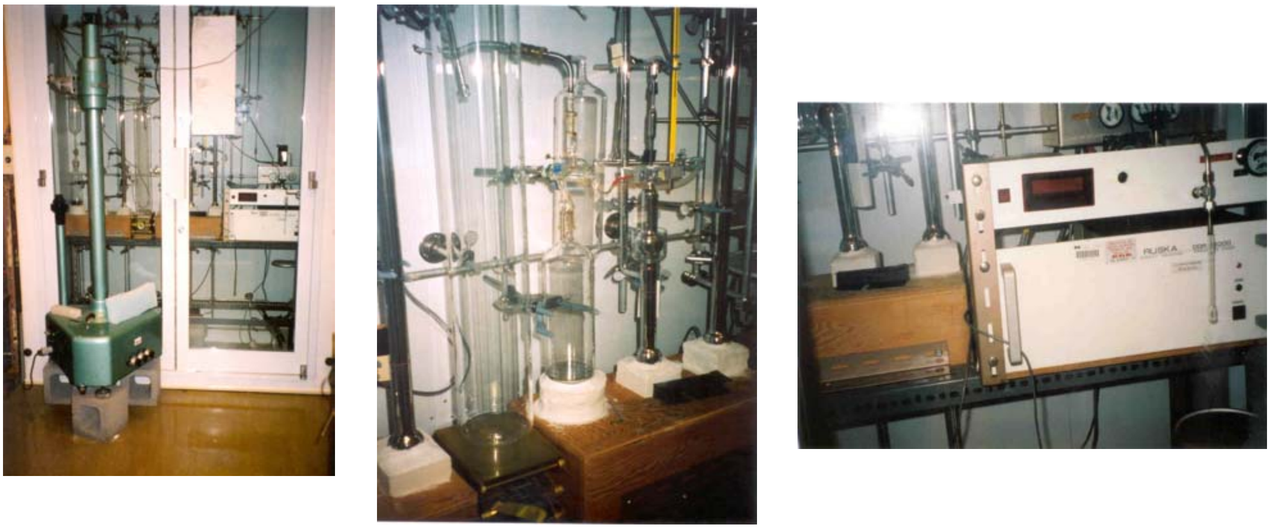

Figure 2: **Manometric facilities showing the Caltech-type cathetometer and manometer chamber (left), a detailed view of the manometer (middle), and Ruska quartz-fibre manometer (right).**

The reference gas samples were provided by the National Oceanic and Atmospheric Administration (NOAA). A test for consistency in CO_2 extracted from a CO_2 in an air standard from a NOAA tank shows a range from 286.12 to 285.03, with an average of 285.43 (Table 1). The values for the NOAA tanks analyzed using the Climate Chemistry Laboratory manometer are shown in Table 2. An inter-calibration with a similar system at the Scripps Institution of Oceanography shows that the Scripps value is on average 0.05% higher than the values determined at the Climate Chemistry Laboratory using the same reference gases. Using CO_2 samples from the Climate Chemistry Laboratory, the sample volume value is 4.5556 cm^3 ±0.035% (about 1 in 3000). The value from the Scripps Institution of Oceanography CO_2 samples is 4.5820 cm^3 ±0.035% (about 1 in 3000). The overall difference of values at the Climate Chemistry Laboratory and the Scripps Institution of Oceanography is ±0.57% or 0.0264 cm^3.

Table 1: **Consistency in CO_2 extractions from a CO_2/air standard for a NOAA tank.**

Test 1	
Date	**Tank # 70124 value (ppm)**
March 18-22, 1988	286.12
March 12-13, 1988	285.14
May 15-17, 1988	285.03
Average	**285.43**

Table 2: Comparison of manometer values (in ppm) measured by the Climate Chemistry Laboratory with values measured by Scripps, for various NOAA tanks.

Test 2	**Tank # 18508**	
Date	**Scripps**	**Climate Chemistry**
November 3, 1983	342.78	–
February 1, 1988	342.89	–
June 5-6, 1988	–	343.14
June 8-9, 1988	–	342.95
June 13-14, 1988	–	342.85
Average	**342.84**	**342.98**
Test 3	**Tank # 18035**	
Date	**Scripps**	**Climate Chemistry**
May 18-19, 1988	335.89	–
May 18-24, 1988	336.21	–
June 2-3, 1988	336.23	–
May 18-19, 1988	–	335.89
May 18-24, 1988	–	336.89
June 2-3, 1988	–	336.28
Average	**336.11**	**336.69**
Test 4	**Tank # 18017**	
Date	**Scripps**	**Climate Chemistry**
November 3, 1983	350.91	–
February 2, 1988	350.93	–
June 21-22, 1988	–	350.92
June 23-24, 1988	–	350.40
June 28-29, 1988	–	350.67
July 5-7, 1988	–	350.49
Average	**350.92**	**350.62**

1.3.2 Conclusion

The Climate Chemistry Laboratory has developed calibration facilities for the production of gravimetric standards and for the calibration of CO_2 standards by manometer. Using standards prepared by NOAA, the consistency of extraction procedures of CO_2 in air standards and the comparison of Climate Chemistry values with the NOAA] assigned values have been presented. Inter-calibration values between Scripps Institution of Oceanography and the Climate Chemistry Laboratory show compatibility between both laboratories.

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1.4 Relating Air-CO_2 Isotope Ratio Determinations to VPDB using Calcite-CO_2 Mixed into CO_2-free Air

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Due to the small changes anthropogenic release of fossil carbon and net terrestrial and oceanic carbon exchange leave in the isotopic composition of atmospheric CO_2, its measurement in ambient air requires the highest precision experimentally obtainable. Moreover, measurements must be comparable between different laboratories at the same high precision level. This has been a challenge in the past, in particular because the international $\delta^{13}C$ scale (VPDB) is based on a carbonate material rather than air, where the highest precision and accuracy are needed. Hence, there is a need for an air reference material strongly linked to VPDB. A rigorous requirement is that the scale be stable over decades and more.

In order to generate such a reliable and long lasting stable isotope ratio standard for CO_2 in samples of clean air, CO_2 is liberated from NBS 19 and other well characterized carbonate reference materials. The gas is then mixed with CO_2-free air. For this purpose we have designed a dedicated acid reaction and air mixing system ('*ARAMIS*'). The layout and experimental details of the carbonate reaction and mixing as well as a host of results have already been described in two earlier reports (Ghosh *et al.*, 2003, 2005). In short, CO_2 is generated by a conventional acid digestion of powdered carbonate in a copper vessel under precise temperature control (± 0.1°C). Evolved CO_2 gas is mixed and equilibrated with a prefabricated gas comprised of N_2, O_2, Ar, and N_2O at close to ambient air concentrations. Distribution into 5L-glass flasks is made stepwise in a highly controlled fashion. The isotopic composition, established using our automated CO_2 extraction/stable isotope measurement systems (Werner *et al.*, 2001), varied within very small margins of error appropriate for high precision air-CO_2 work (about ± 0.015 ‰ for $\delta^{13}C$ and ± 0.025 ‰ for $\delta^{18}O$). For establishing a valid $\delta^{18}O$ relation to the VPDB scale, the temperature dependence of the reaction between 25°C and 47°C had to be determined with the correspondingly high level of precision for the first time (Ghosh *et al.*, 2003, 2005).

CO_2-in-air mixtures were generated from a selection of reference materials:

- The material defining the VPDB isotope scale (NBS 19, $\delta^{13}C$ = +1.95 ‰ and $\delta^{18}O$ = -2.2 ‰ exactly).
- A local calcite similar in isotopic composition to NBS 19 ('MAR-J1', $\delta^{13}C$ = +1.97 ‰ and $\delta^{18}O$ = -2.02 ‰).
- A natural calcite with isotopic compositions closer to atmospheric values ('OMC-J1', $\delta^{13}C$ = -4.24 ‰ and $\delta^{18}O$ = -8.71 ‰).

NBS 19 was used to anchor the local CO_2-in-air scale to VPDB. Over the course of more than 2 years more than seven separate preparations of NBS 19 were made with sample amounts between 40 and 60 mg each, resulting in a total of 21 5L-flasks filled with artificial air. The corresponding measurements had a precision of 0.012 ‰ for $\delta^{13}C$ and 0.015 ‰ for $\delta^{18}O$ (inter-batch). They also served to assign high precision stable isotope values to the other carbonates. The text box (Figure 1) lists the properties of the relevant carbonate materials. The criteria for their selection were to have one local reference material resembling NBS 19 as closely as possible in isotopic composition as well as all other properties which could possibly play a role in the isotopic composition of the extracted CO_2. The second carbonate should be largely identical to the first except for the isotopic composition, this time the latter should produce CO_2 gas close to atmospheric values. Unfortunately, natural calcites with this composition which also fulfill the requirement of high purity, homogeneity, low organic carbon etc. are extremely rare and difficult to find.

MAR-J1 and OMC-J1 Calcites:

Laboratory carbonate reference materials were prepared from a (limestone) marble slab **('MAR-J1', Marble-Jena #1**) purchased from a local vendor and from a calcite slab from the Meieberg section of the Otavi platform in northern Namibia **('OMC-J1'; Otavi Meieberg Calcite-Jena #1**), which was kindly provided by Paul Hoffmann. The slabs were broken into chips, crushed into fine grains, and sieved into fractions.

MAR-J1:

^{13}C: 1.97 ‰; ^{18}O: -2.02 ‰ VPDB

The <250 µ size fractions weighing about 900 g was labeled 'MAR-J1'. Texture and appearance of the powder is similar to NBS 19 carbonate material. Other fractions, 250-315 µ (~500 g) and 315-400 µ (~300 g), were designated as 'MAR-J2' and 'MAR-J3' and stored for future use. Quantitative analysis using ICP-MS and ICP-OES indicated an **average $CaCO_3$ content of 98.0 % and 2.0 % $MgCO_3$. Al, Fe, Cu, Mn, Na, K together were less than 0.1 %.** NBS 19 (TS limestone) is very similar: in line with literature XRF data we obtained 98.1 % $CaCO_3$ and 1.8 % $MgCO_3$. Other elements were 0.08 % in total. The similarity of the two materials is further confirmed by observing the carbonate reaction yield with NBS 19 and MAR-J1 resulting in the same amounts of CO_2 gas.

OMC-J1:

^{13}C: -4.4 ‰; ^{18}O: -8.4 ‰ VPDB (final batch)

The composition analysis of the Otavi-Meieberg calcite using ICP-AES and ICP-OES has given **98.7 % $CaCO_3$ and 0.9 % $MgCO_3$ with non-carbonate cationic impurities summing up to 0.4 %.** The crushing, milling and sieving left us with 1270 g powder with a grain size <100 µm ('OMC-J0'), 700 g between 100 and 200 µm ('OMC-J1') and 1800g between 200 and 400 µm ('OMC-J2/3'). In order to avoid oxygen exchange with ambient moisture or CO_2 all fractions are kept in glass or PE jars topped with Ar.

Figure 1: **Properties of the calcite materials used for preparing CO_2 in the JRAS (Jena Reference Air Sets) activities.**

Using Mar-J1 and OMC-J1 we have so far produced a total of nine different JRAS (Jena Reference Air Sets)-sets comprising two 5L-borosilicate glass flasks each, filled with artificial air to a pressure of 1.6 Bar (see Figure 2). In addition, a limited number of similar sets have been prepared using pure CO_2 reference gases (Oberlahnstein and Pflanzen) for mutual laboratory scale control with the Stable Isotope Laboratory at the University of Heidelberg (I. Levin, UHEI). This has enabled to examine an extra set of controls in particular for tracing isotopic alterations in CO_2 related to the extraction procedure and to the N_2O correction.

- pair of 5-L glass flasks
- pressure = ~ 1.5 Bar
- single valve, PCTFE seat
- fits to most sample ports
- transport friendly Al- case
- refill possible
- 12 months guarantee for $\delta^{18}O$

Figure 2: **A JRAS-set comprises two 5L-glass flasks with artificial air at initially 1.6 Bar. The CO_2 in the flask air is produced from the MAR-J1 and OMC-J1 calcite powders.**

For each of the 5L-flasks we determined the CO_2 and N_2O mixing ratios as well as the resulting isotopic composition of CO_2. The data were then used to assign a certified isotopic composition to each flask generated from the average of the 3 flasks prepared in one batch. The intra-batch precision was indistinguishable from the long term measurement precision, and a difference between flasks prepared in a single batch has not been detected so far. The isotopic compositions of the JRAS-sets as determined and anchored to VPDB using NBS 19 at BGC-IsoLab are used to construct a rigid long term link and quality control of the Jena air-CO_2 stable isotope scale (see Figure 3).

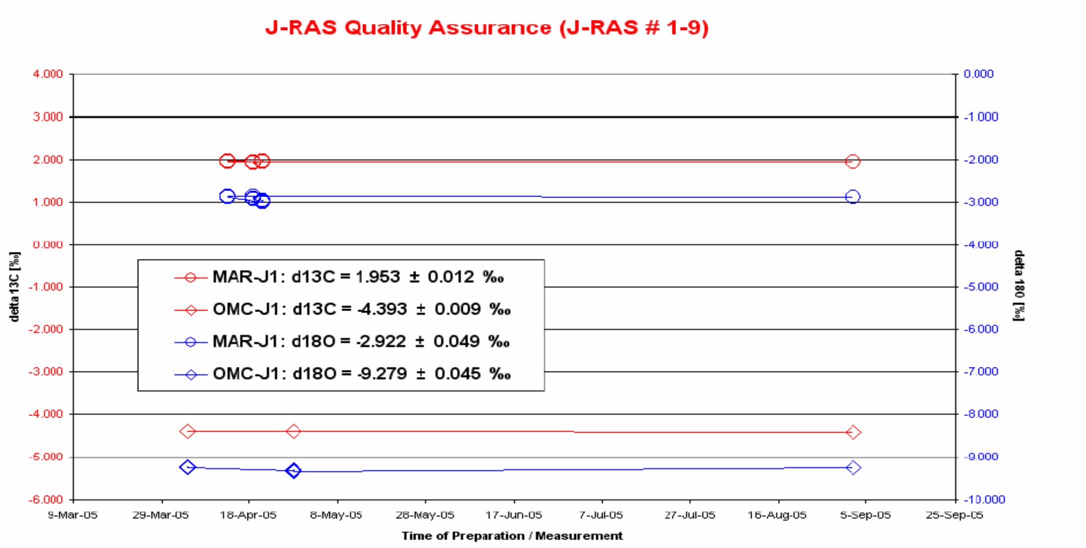

Figure 3: **Quality assurance performance record (to be continued into the foreseeable future). This graph provides the long term traceability of JRAS reference air to VPDB.**

Six of the nine JRAS-sets have been sent to participating laboratories. As a first experiment an intercomparison exercise was conducted, comparing results from the JRAS-set as determined on the locally established stable isotope ratio scales. So far, four of the six laboratories have sent us results, which are graphically shown in Figure 4.

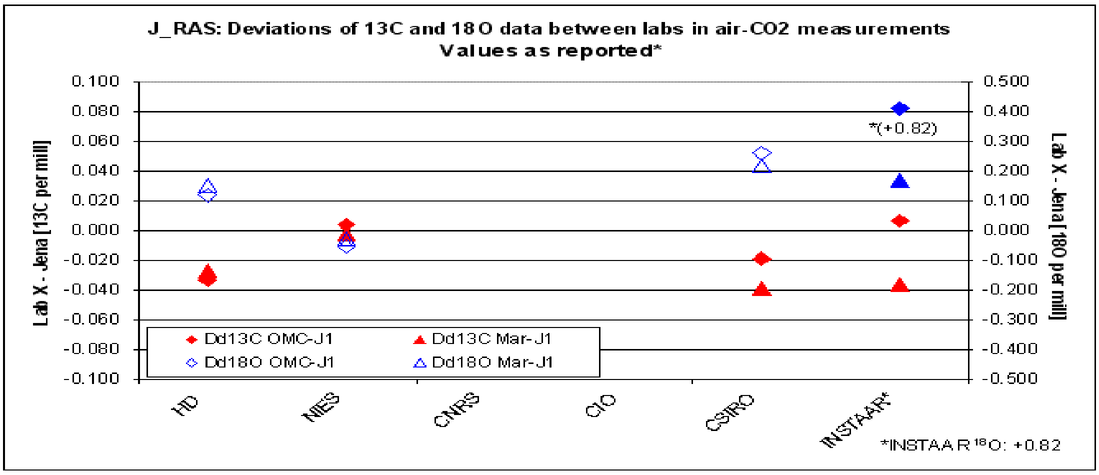

Figure 4: **Results from a first inter-laboratory comparison of the JRAS gases with the results expressed on the respective locally established anchor to the VPDB scale. The original INSTAAR δ^{18}O results have been shifted by +0.82 per mill (J. White, personal communication).**

The average deviation of the reported $\delta^{13}C$ values relative to the BGC IsoLab value is -0.019 ‰. This can be further improved to -0.002 ‰ by adjusting the ^{17}O correction to a common parameter set (Assonov *et al.*, 2003; Verkouteren and Klinedinst, 2004). The corresponding precision is 0.019 ‰, close to but not quite at the target net precision accepted by WMO/IAEA (0.01 ‰, see Expert Group Recommendations of the 13th WMO/IAEA CO_2 Experts Meeting). The values for $\delta^{18}O$ were much inferior (not unexpected) with the average at +0.181 ‰ and a precision of 0.141 ‰ vs. VPDB (gas). The discrepancies have multiple components including different scales arising from possible offsets in the preparation of CO_2 from NBS 19 as well as fractionation effects during the extraction procedure requiring more detailed work in the participating laboratories for further elucidation (Werner *et al.*, 2001).

In order to exclude alteration of the $\delta^{18}O$ value during storage in the JRAS flasks as a further source of isotopic variation we have extensively studied the behavior of CO_2 in air inside 1L-borosilicate flasks over time. In a previous report (Rothe *et al.*, 2003) we have shown that the alteration is unidirectional with $\delta^{18}O$ decreasing monotonically over time at a rate of -0.5 ‰ per year. This finding was independent of the polymer used for sealing (PCTFE and PFA). We now have studied the behavior of $\delta^{18}O$ as a function of temperature, pretreatment, glass type and time. Figure 5 shows the most important results: With a special flask pretreatment, keeping them at elevated temperature (+60°C) for an elongated time (72 hours) while pumping (0.5 mBar), the previously observed fast decline of $\delta^{18}O$ vanished to a large extent. The figure shows storage results for borosilicate flasks kept in storage at 60°C for up to 200 days. Under these conditions the observed alterations had been as bad as -1.5 ‰ per annum previously. Also depicted in Figure 5 are similar results using all-quartz flasks (also with PCTFE seats) which did not exhibit a change in the $\delta^{18}O$ signature over a full year of storage at this elevated temperature. From this observation we conclude that exchange with H_2O at the glass surface is probably responsible for the $\delta^{18}O$ alteration over time with water being slowly released from inside the boro-silicate glass to the surface and the gas phase via diffusion.

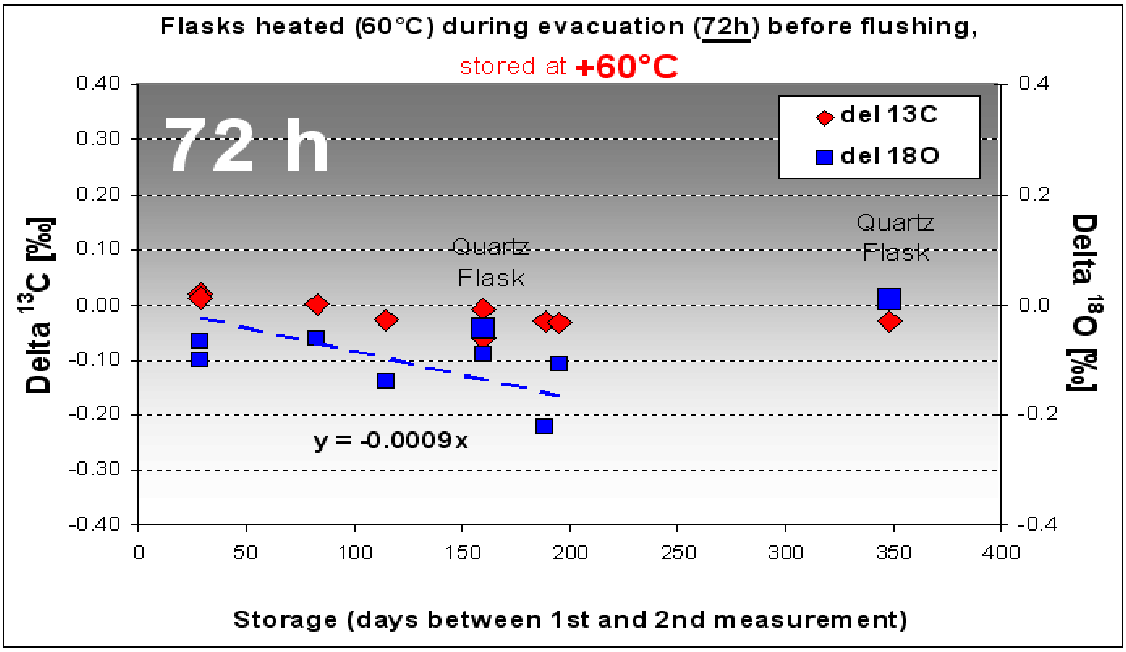

Figure 5: Alteration of $\delta^{18}O$ of CO_2 in air as a function of storage time in 1L-borosilicate and in 1L-quartz flasks.

The JRAS flasks have all been treated in this fashion (pumping for 72 hours at 60°C) as well. Here, the volume to surface ratio is more favorable than in the 1L-flasks, rendering a $\delta^{18}O$ alteration over time at ambient temperatures even less likely. The 5L-flasks have been tested for these and other deleterious effects during long term storage of air over more than 200 days. The results are presented in Figure 6. Both, $\delta^{18}O$ and $\delta^{13}C$ isotopic ratios are independent of the storage time with an overall precision which is indistinguishable from other short- and long term high pressure cylinder or flask measurements using the same equipment, confirming the suitability of the 5L-flasks as storage vessels for reference air in inter-comparison exercises.

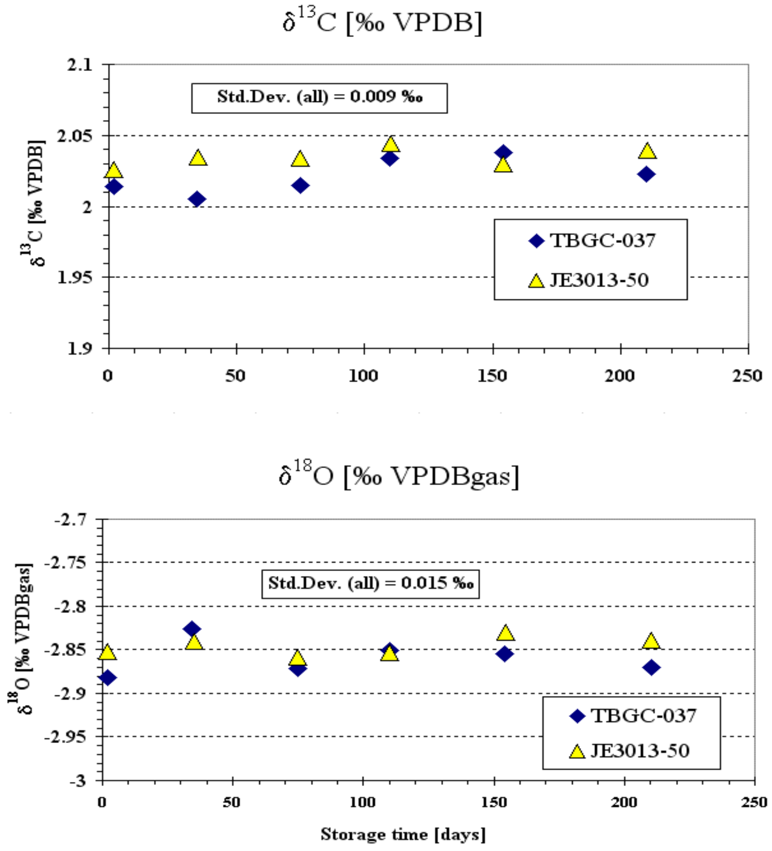

Figure 6: **Effects of long term storage on the isotopic composition of CO_2 in air inside 5L-flasks.**

Acknowledgments

The initial work was made by P. Ghosh and M. Patecki. The fruitful contributions by Ingeborg Levin are gratefully acknowledged. The mixing ratios were determined by Armin Jordan.

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1.5 About Disagreements in Inter-Comparison Activities of Isotope Ratio Measurements for CO_2

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1.5.1 Introduction

The carbon stable isotope ratio of CO_2 is a useful tracer to study the CO_2 budget in the atmosphere. The World Meteorological Organization (WMO) and International Atomic Energy Agency (IAEA) have recommended an inter-laboratory comparability and precision (see Recommendations section for definitions) for atmospheric CO_2 isotope measurements of 0.01 per mil for carbon and 0.05 per mil for oxygen, respectively (WMO, 2001). In general, because each laboratory uses its own sample extraction method, standardization scheme, and analytical instrument, inter-comparison exercises between different laboratories are a useful tool to discover, compare, and discuss differences in the respective scales for reporting stable isotope ratios.

Two pure CO_2 gases, NARCIS-I and NARCIS-II (NIES Atmospheric Reference CO_2 for Isotope Studies) were produced at NIES (Mukai, 2005) specifically for use in inter-comparison activities. The isotopic composition of NARCIS-I is close to that of CO_2 in air, as are GS-19 and GS-20, which are distributed by the University of Groningen, The Netherlands (Meijer, 1995). The isotope ratio of NARCIS-II was adjusted to a value close to that of CO_2 produced from NBS19 carbonate, which is the primary standard reference material for carbon and oxygen stable isotope ratios and is distributed by both the IAEA, Vienna, Austria, and The National Institute for Standards and Technology, Washington, USA. Usually a small amount and limited sample number of NBS19-CO_2 is produced in each laboratory. On top of this each batch may have a small variation in isotope ratio. Hence, it is difficult to use lab-made NBS19-CO_2 itself for high precision inter-comparison work. Instead, comparison by using a CO_2 gas similar to NBS19-CO_2 (like NARCIS-II) is expected to provide an alternative to improve accuracy in comparing NBS19-CO_2 prepared by different laboratories. In other words: We will be able to check the “zero” point of the VPDB scale between laboratories by using NARCIS-II. On the other hand, the NARCIS-I comparison will allow us to discover and quantify biases arising from specific analytical conditions such as cross contamination inside the mass spectrometer when atmospheric samples are measured.

In addition to inter-comparison with pure CO_2, air samples have been used in such studies in order to match more closely the nature of the samples. University of Heidelberg (UHEI) within the TACOS and Carbo-Europe-IP projects has conducted inter-comparison of identical air in different glass containers prepared in “Sausages”. The "Melon" exercise using 34L stainless steel containers (ESSEX Co.) filled with air at low pressure (below 4 bar) was initiated by CSIRO (Allison et al. 2003; Schmidt et al, 2003; Langenfelds et al. 2005). Three “Melons” have been passed between CSIRO and Japan (NIES and Tohoku Univ.) once per year. The NOAA ESRL Carbon Cycle Greenhouse Gases group (formerly NOAA-CMDL) has provided us with gas standards that have stable isotope values assigned to the CO_2 by the Institute of Arctic and Alpine Research (INSTAAR) at the University of Colorado (CU). Recently the IsoLab group at the Max Planck-Institute for Biogeochemistry in Jena (MPI-BGC) produced CO_2 from carbonate standards mixed into CO_2-free air (Jena-Reference-Air-Set) for inter-comparison (Ghosh et. al., 2005).

In this work, the results of inter-comparison activities in recent years using NARCIS-I and NARCIS-II are compared and the cause of local scale differences are discussed. Also, NARCIS results are compared to other inter-comparison work using air samples.

1.5.2 Evaluation of Scale Differences in the NARCIS Inter-Comparison

Until present, seven laboratories have provided both NARCIS-I and NARCIS-II data. By using these data, the causes of differences in the isotope scales between laboratories can be preliminarily evaluated. However, as the data are not yet fixed, the results may not allow us to draw firm conclusions for each laboratory.

First, NARCIS-II data are expected to show variations in the laboratory “zero points”, made through CO_2 prepared individually from NBS19 carbonate. Second, the delta difference between NARCIS-I and NARCIS-II was considered to have a relation with the “span” component during mass spectrometric analysis. Therefore, the possible cause of measured differences between laboratories for NARCIS-I could be split into the zero-point offset and the span deviation by comparing these values.

As shown in Table 1, the range (max-min) of the C and O isotope ratios for reported NARCIS-II data were 0.03 per mil and 0.1 per mil respectively. Clearly, O isotope ratios show a larger range in the data, implying an experimental cause during the first step of calibration for the $^{18}O/^{16}O$ ratio. For the carbon isotope ratio, 0.03 per mil is slightly beyond the precision recommended (see Recommendations section). The distance between NARCIS-I and NARCIS-II in C and O isotope ratios showed ranges of 0.07 and 0.09 per mil respectively.

In this work, for simplicity, the averages of C and O isotope ratios reported for NARCIS-I and NARCIS-II have been set as working anchors (AVG(I) and AVG(II)). We apply an offset adjustment to the NARCIS-I data by subtracting the difference of each NARCIS-II value from the average (= (II) - AVG(II), where ‘(I)’ or ‘(II)’ refer to an individual laboratory’s measurements of NARCIS I and II, respectively). The adjusted NARCIS-I data show a substantial improvement in standard deviation (SD) of δ^{18}O data (from 0.060 to 0.028 per mil), as shown in Table.1. Therefore, this zero-point offset adjustment can improve inter-comparability and help reach the recommended target intercomparability. However, in the case of δ^{l3}C a similar adjustment increased the SD from 0.017 to 0.025 per mil. Hence, we suggest that in this case the cross contamination (or eta-effect) affected the δ^{13}C measurement considerably.

Table 1. Tentative stable isotopic composition assigned to NARCIS-II and the effect of NARCIS-II adjustment on reported values of NARCIS-I. All values are reported in per mil.

Sample	NARCIS-II				NARCIS-I		(I) - (II)		Offset adjusted NARCIS-I#	
Institute	δ^{13}C	SD	δ^{18}O	SD	δ^{13}C	δ^{18}O	δ^{13}C	δ^{18}O	δ^{13}C	δ^{18}O
NIES	1.927	0.005	-2.589	0.013	-8.556	-0.729	-10.483	1.860	-8.558	-0.693
Tohoku U	1.945	0.009	-2.573	0.018	-8.550	-0.681	-10.495	1.892	-8.570	-0.662
MPI-BGC	1.923		-2.635		-8.578	-0.746	-10.500	1.889	-8.591	-0.662
MPI-Chem	1.914	0.023	-2.554	0.022	-8.557	-0.630	-10.472	1.923	-8.546	-0.630
Univ. Bern	1.917	0.006	-2.588	0.016	-8.532	-0.753	-10.450	1.835	-8.524	-0.718
U.Heidelberg.	1.918	0.019	-2.480	0.018	-8.535	-0.608	-10.453	1.872	-8.528	-0.681
EC/ASTD	1.919	0.011	-2.488	0.020	-8.538	-0.606	-10.457	1.883	-8.532	-0.671
AVG	1.923		-2.558		-8.549	-0.679	-10.475	1.879	-8.550	-0.674
Standard dev	0.010		0.056		0.016	0.065	0.021	0.027	0.025	0.028
RANGE&	0.031		0.155		0.045	0.147	0.051	0.088	0.066	0.088

Note: All laboratories reported δ^{13}C and δ^{18}O calculated using the procedure recommended by Allison et al. (1995) or Craig method. Therefore, differences based on the calculation are considered to be small.

#: The offset is ((II)-AVG(II)). The adjusted value for NARCIS-I = (I)-((II) – AVG(II))

&. Range is Max-Min.

Because the difference (NARCIS (I) - (II)) exhibits a large variation (0.07 per mil for δ^{13}C and 0.09 per mil for δ^{18}O), the "span" effect must contribute significantly to the scale difference for each laboratory. When we use the difference of the averages of NARCIS-I and NARCIS-II (i.e. AVG(I) - AVG(II)) as a "span" reference, we can estimate the relative degree of cross contamination effect for each laboratory as ((I) - (II)) - (AVG(I) - AVG(II)). By doing this, the overall deviation of NARCIS-I from the average (I) – AVG(I)) can be separated into two components, a "zero" offset and a "span" difference, as shown in Table 2. Figure 1 is a graphical presentation of the contributions from the "zero" offset and the "span" difference to the overall difference of NARCIS-I from the average data. The figure indicates that the "span" difference, which corresponds to the cross contamination effect, contributes more to the overall difference in δ^{13}C while the "zero" offset difference may be more responsible for the overall difference for δ^{18}O.

If cross contamination is a main cause of the "span" deviation ((I) - (II)), the absolute measured difference tends to be too small. Hence, the larger absolute values of ((I) – (II)) are likely to be closer to the true value. In addition, because the cross contamination effect for δ^{18}O must correlate with that for δ^{13}C (Meijer et al., 2000), the deviation of the "span" from truth for both δ^{13}C and δ^{18}O should show up in a similar fashion. However, this is not our observation and our largest absolute values of the "span" ((I) - (II)) for δ^{13}C and δ^{18}O are from different laboratories; MPI-BGC gave the largest value for δ^{13}C (10.500 per mil), but the largest value for δ^{18}O (1.923 per mil) was reported by MPI-Chem. The second largest values were reported by Tohoku University for both isotope ratios. But the third largest values were given by NIES for δ^{13}C and MPI-BGC for δ^{18}O. If all the measurements were made in a systematic and consistent fashion, such a tendency is not explained easily. On the other hand, if a multiple-point standards scheme has been used to measure samples (e.g. during span correction), a systematic cross contamination effect may be difficult to examine in this work. Also, because the data for both samples were not measured at the same day in each laboratory, measurement conditions may not be completely identical for both NARCIS-I and NARCIS-II. Therefore, analytical precision may influence the results. Finally, the δ^{18}O difference between NARCIS-I and NARCIS-II is smaller than the δ^{13}C difference between them and the "span" effect may thus be harder to determine.

Table 2: The contributions of "zero" offset and "span" difference to the overall difference for NARCIS-I data reported in each laboratory from the average. All values are in per mil.

	Overall difference		"zero" offset		"span" difference*	
Equation	(I)-AVG(I)		(II)-AVG(II)		Overall difference – "zero" offset	
Institute	δ^{13}C	δ^{18}O	δ^{13}C	δ^{18}O	δ^{13}C	δ^{18}O
NIES	-0.006	-0.050	0.004	-0.031	-0.010	-0.019
Tohoku U	-0.001	-0.002	0.022	-0.015	-0.022	0.012
MPI-BGC	-0.028	-0.067	-0.001	-0.077	-0.028	0.010
MPI-Chem	-0.008	0.049	-0.009	0.005	0.001	0.044
Univ. Bern	0.017	-0.074	-0.006	-0.030	0.023	-0.044
U.Heidelberg.	0.014	0.071	-0.005	0.078	0.020	-0.007
EC/ASTD	0.012	0.073	-0.004	0.070	0.016	0.003
AVG	0.000	0.000	0.000	0.000	0.000	0.000
Standard dev	0.016	0.065	0.010	0.056	0.021	0.027
RANGE[&]	0.045	0.147	0.031	0.155	0.051	0.088

** "span" difference = ((I)-AVG(I)) – ((II)-AVG(II)) &. Range is Max-Min.*

1.5.3 Relation to Other Inter-Comparison Activities

Sausage and Melon samples used in the intercomparison activities, as well as JRAS, are synthetic mixtures of CO_2 in air prepared using different procedures (e.g., *Allison et al.*, 2002; *Schmidt et al.*, 2003; *Ghosh et al.*, 2005). As such, a correction for the presence of N_2O, which contributes to the measured ion currents, is necessary in order to calculate the pure CO_2 isotope ratios. At first, we checked the N_2O correction algorithm used at NIES. Although we had employed experimentally determined correction parameters, some biases were considered possibly owing to the isotope ratio of CO_2 used and to the precision of the mixing ratios of N_2O and CO_2. However, during the JRAS comparison, inconsistencies arising from our N_2O correction were found to contribute to the observed differences more than expected. Therefore, to improve the N_2O correction, we use the mass sensitivity ratios of 45/44 and 46/44 for N_2O from Ghosh and Brand (2004) for our mass spectrometer. The parameters of the N_2O correction for this comparison are as follows.

New correction for $\delta^{13}C$(‰) = 0.250 x N_2O(ppb) / CO_2(ppm) (previously: 0.182 ‰ ppm / ppb)

New correction for $\delta^{18}O$(‰) = 0.357 x N_2O(ppb) / CO_2(ppm) (previously: 0.235 ‰ ppm / ppb)

Using these new corrections significantly improves the consistency of the NARCIS and JRAS comparisons between NIES and MPI-BGC (Figure 2). NARCIS and JRAS are both based on pure CO_2. Therefore, similar scale differences in C and O isotope ratios between NIES and MPI-BGC should be found in both NARCIS and JRAS.

To compare the "Sausage" results, the data from MPI-BGC were corrected from the original assignment (”CG-99”) to the JRAS scale to obtain scale consistency. For C isotope ratio, 0.072 per mil (Ghosh et al., 2005) was subtracted from the data but no adjustment was made for the O isotope ratio. Sausage data from NIES, MPI-BGC and UHEI are compared together with NARCIS and JRAS in Figure 2. The $\delta^{13}C$ differences in NARCIS and JRAS during NIES, MPI-BGC and UHEI inter-comparisons were small (< 0.03 per mil), despite the fact that NARCIS-II and one of the JRAS gases had a much heavier carbon isotope ratio than ambient air. On the other hand the difference in "Sausage" between NIES and UHEI was about 0.05 per mil, showing that the deviation between the two was slightly larger than that for pure CO_2. (Note that the NIES scale here is tentatively changed by the new N_2O correction; comparison results from earlier reports from UHEI show different values). In the case of MPI-BGC, the "Sausage" data show a deviation close to that for NARCIS-I (0.04 per mil) but with some variability.

If we compare the results of "Sausage" with "Melon" and our NOAA cylinder, they exhibit consistent relations between CSIRO, CU and NIES, suggesting that their scales for air samples have been constantly maintained. NIES showed about 0.04 per mil lighter in $\delta^{13}C$ than data from CSIRO (also CU), and this is shown as minus 0.04 per mil in Figure 3. "Sausage" data had relatively larger variation than "Melon" and the NOAA cylinder (30L), possibly because the air volume of "Sausage" was much smaller and the values may be more easily affected by any contamination or distortion. However, the scale difference for air samples seems to be different from that for pure CO_2 (NARCIS-I). In the case of NARCIS-I data, the difference between NIES and CSIRO was plus 0.03 per mil as shown in Figure 3, suggesting that about 0.07 per mil may come from the scale difference between the pure CO_2 scale and the air standard scale (CG99) used in CSIRO. CSIRO has recently revised their CG99 scale to a new scale that reduces the difference between the “Melon” data and NARCIS-I, (air sample and pure CO_2) from 0.07 to 0.03 per mil in $\delta^{13}C$. As for Tohoku University, because the scale differences from NIES were initially small, about 0.01 per mil in $\delta^{13}C$, the revised NIES scale increases the difference to about 0.05 per mil as shown in Figure 3.

For oxygen isotope ratios, similar results to carbon isotope ratio were obtained (Figures 4 and 5). However, the variation in the "Sausage" comparison was considerably larger than that for carbon. This origin of this variation is neither analytical precision in IRMS measurement nor extraction procedure. At NIES, CO_2 was independently extracted twice from the "Sausage" flask and analysis from these extractions showed only small variation, usually below 0.03 per mil in $\delta^{18}O$.

The MPI-BGC group has reported that the usual (Borosilicate) glass flask has the potential to change the CO_2 oxygen isotope ratio of a stored air sample over time (Rothe et al, 2005). In this work, we confirm the finding that during storage the CO_2 oxygen isotope ratio can be dramatically altered in 1L flasks. Using a newly developed vacuum line for dilution of pure CO_2, NARCIS-I was diluted with zero air in the 1L glass flask to give a concentration of about 350 ppm. As a pre-treatment, the 1L flasks in NIES for this work and the "Sausage" inter-comparison were usually evacuated over night at 50°C before use and then pressurized with dry air. The flask is equipped with two glass valves with Viton O-ring seals at both ends. Several such samples were prepared and isotope ratios were measured periodically over a 4-month period. Figure 6 shows the measured water content in the 1 L flasks (and also in the Sausage flasks) as a function of the storage time. (H_2O was estimated from the water pressure measurement at the CO_2 extraction procedure as water is also trapped in the procedure). Clearly, the water content increases over time. We suspect that water entered the flask by permeation through the Viton-O ring of the glass valve (Sturm et al., 2004). If so, air humidity in the storage area might affect the rate of permeation and, therefore, water content inside the flask.

The NARCIS-I dilution experiment reveals that oxygen isotope ratios decrease significantly with time, possibly related to the water content increase (Figure 7). The decrease of the O isotope ratio seems to be correlated more with the amount of water content in the sample rather than storage time (Figure 8). Because humidity in the storage room was not controlled (it is relatively humid during summertime in Japan), the water content in "Sausage" flasks showed clear seasonal variation (Figure 9). In wintertime, water concentration was low and the difference between NIES and MPI-BGC (or UHEI) was much smaller than in other seasons. The difference in winter samples was apparently close to the NARCIS-I results, suggesting that if we can keep the sample dry, the variation will become much smaller and the result will come close to that from the comparison using pure CO_2.

Although the MPI-BGC group (Ghosh et al. 2005) suggested that longer evacuation time under higher temperature before usage of glass flasks can improve stability of isotope ratios inside, the reason why even very low water content (e.g. 200 ppm) can still affect the O isotope ratio in a small glass flask is not clear and needs further attention. The origin of the water could be the air and/or glass. Is water the prime cause of the alteration in oxygen isotope ratio? In our experiment, a few flasks showed only a small response in oxygen isotope ratio by increasing the water concentration during storage (Figures 7 and 8), although we also have to take into consideration the individual flask characteristics. Because such a low content of water usually cannot affect the oxygen isotope ratio directly in gas phase, the water concentration increase and the alteration of the oxygen isotope ratio may be independent phenomenon. However, if this is the case, we have to find a reason for the apparently good agreement in oxygen isotope ratio between NIES and MPI-BGC (or UHEI) during wintertime.

1.5.4 Conclusions

The NARCIS-I and II comparison has provided useful information about underlying features of isotope ratio scale differences between participating laboratories and includes hints about the origins of these differences. The primary difference for oxygen isotope ratios seems to be the zero-point of the local NBS-19-CO_2 scale produced in each laboratory. Provided the oxygen isotope ratio of NARCIS-II can be determined with sufficient accuracy, it may be used to unify the $\delta^{18}O$ scale at the required WMO/IAEA target precision. The situation for the measurement of carbon isotope ratios seem more complicated. Cross contamination is probably the major component of the observed scale differences, and it is likely that this changes with time and condition of the measurements. Therefore, use of an accurately calibrated and at the same time convenient reference sample such as NARCIS-I may be key to a unified $\delta^{13}C$ scale in the future.

Inter-comparison activities using air samples such as "Sausage", "Melon", and JRAS provide an opportunity for a high quality comparison between pure CO_2 and CO_2-in air. In terms of atmospheric CO_2 stable isotope measurements, this type of intercomparison activity may be a more practical approach to establish a reliable scale. We have observed acceptable correlation between the different scales from individual laboratory, despite that air in small flasks exhibited relatively larger variation than the air in larger volume containers. A special problem is the observed change of oxygen isotope ratio over time inside our 1L flasks. As a consequence, data from flask sample measurements need a careful consideration of the particular experimental conditions and possibly post-measurement treatment of the data to make a firm comparison.

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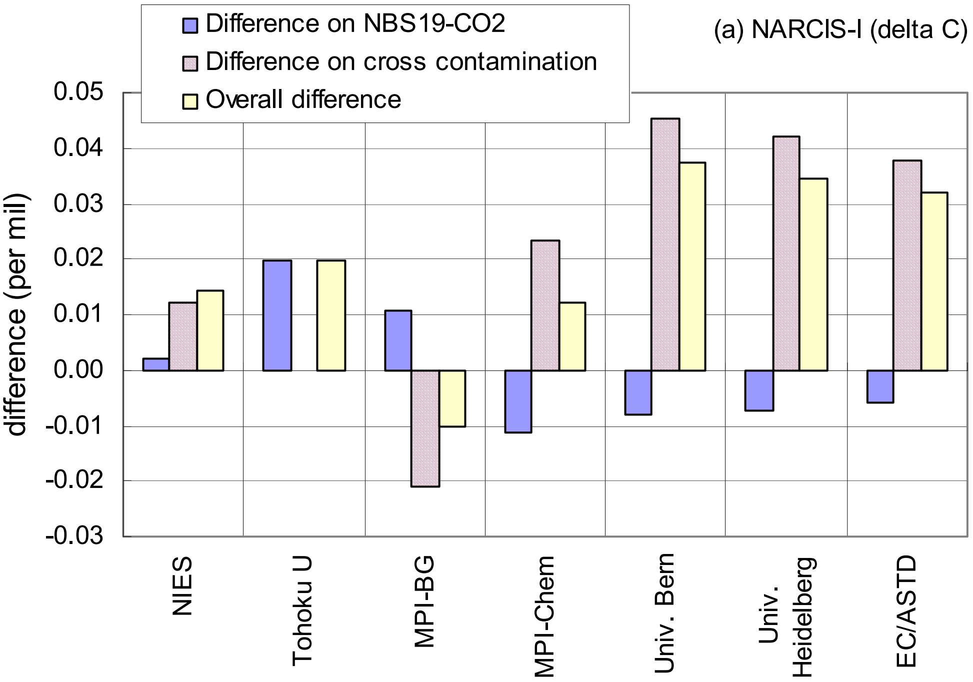

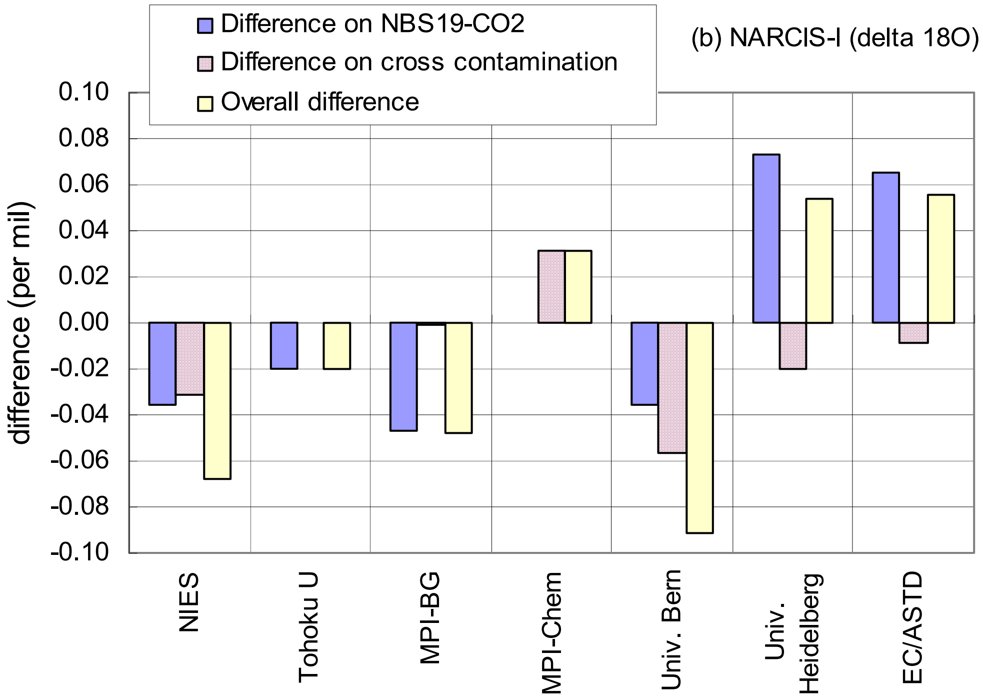

Figure 1: **Representation of the "zero" offset and "span" difference contributions to the NARCIS-I differences reported by the seven laboratories, estimated by (II)-AVG(II) and ((I) – (II)) - (AVG(I)-AVG(II)), respectively.**

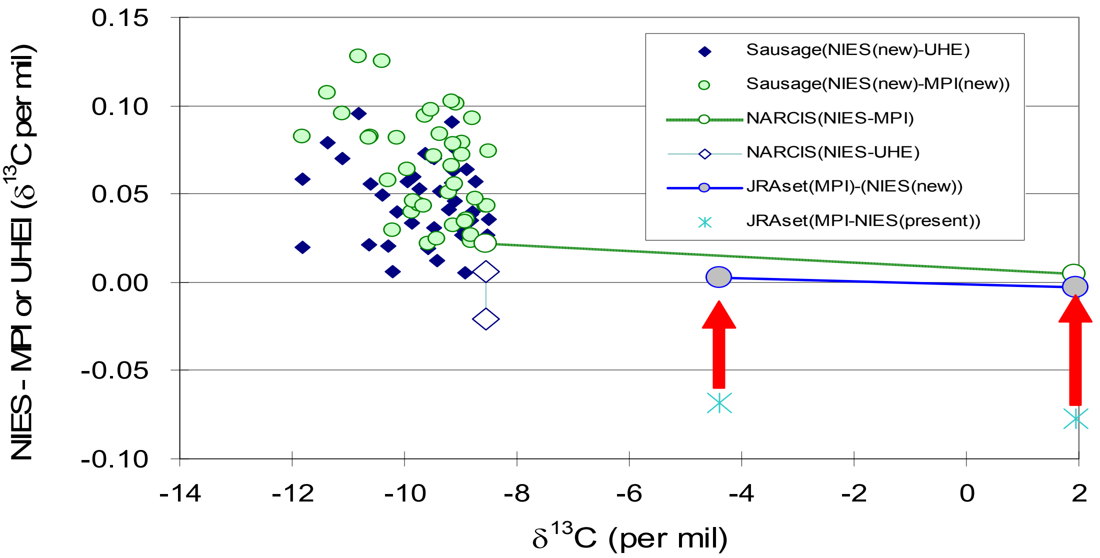

Figure 2: Observed $\delta^{13}C$ differences between NIES, MPI-BGC, and UHEI from 3 intercomparisons.

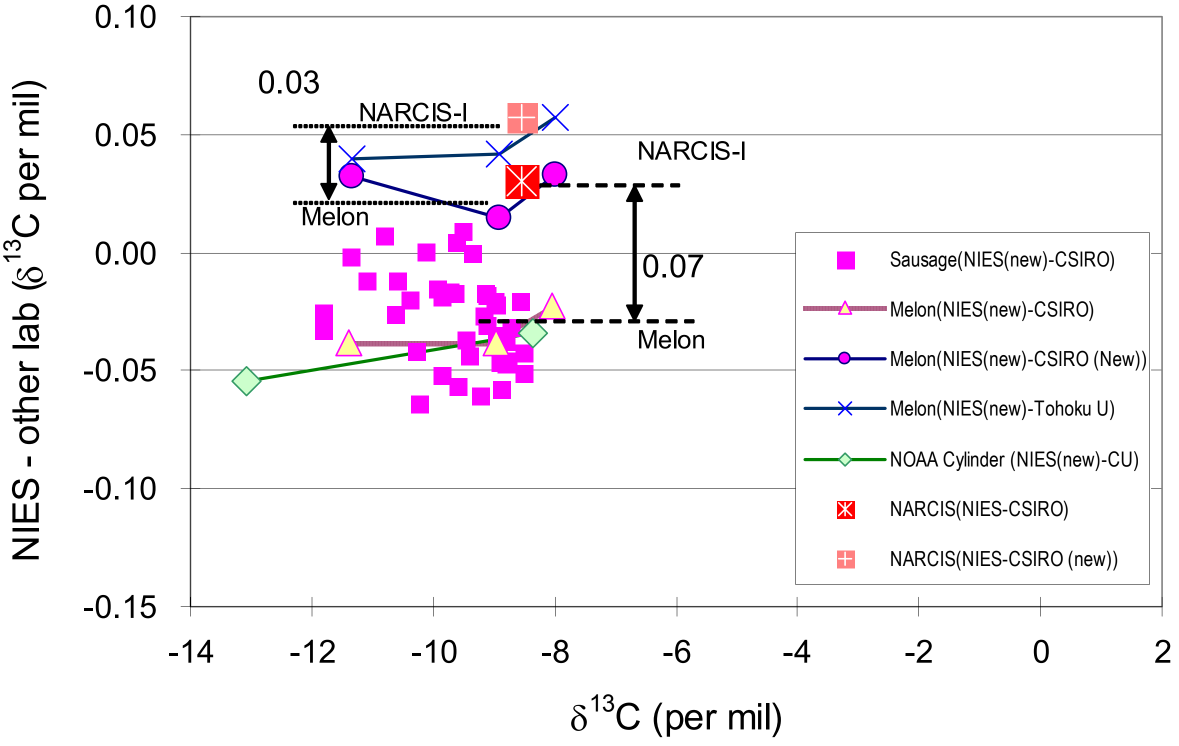

Figure 3: Observed $\delta^{13}C$ differences between NIES and CSIRO, Tohoku University, and UC from 4 inter-comparisons. The new "Melon" and NARCIS-I data comparisons are also shown here. As a consequence of the CSIRO scale revision, observed differences between air samples and pure CO_2 have become smaller.

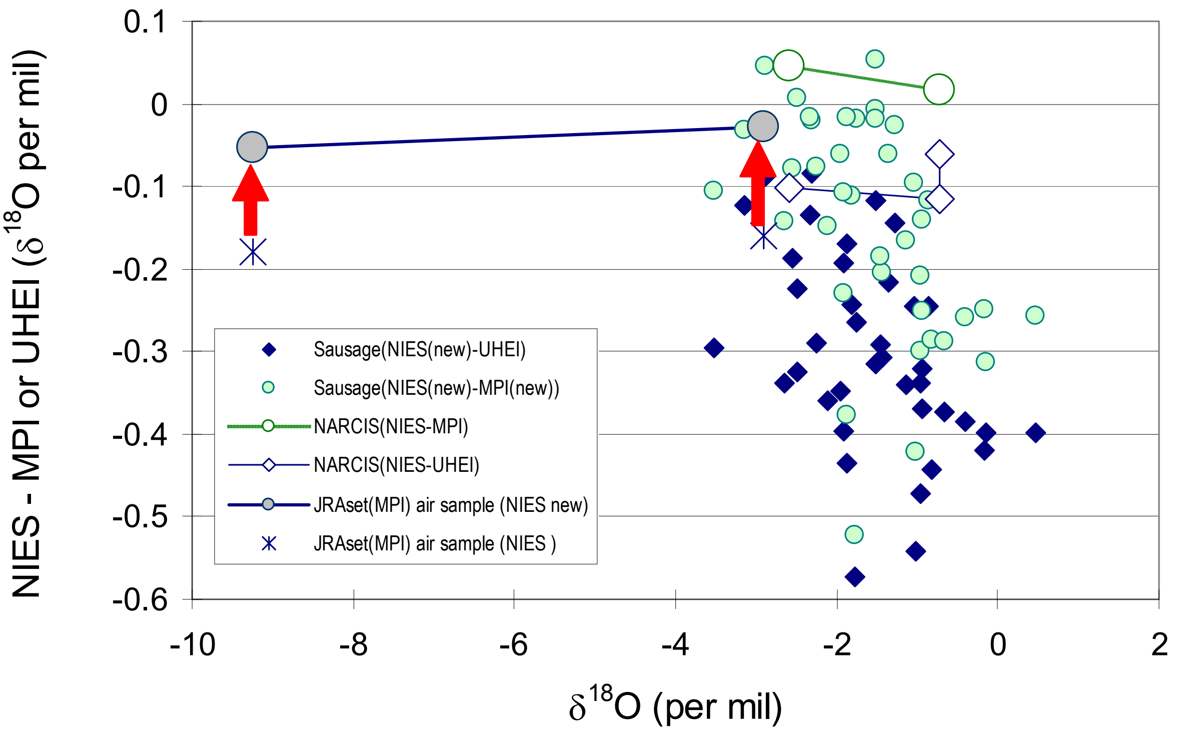

Figure 4: Observed δ^{13}C differences between NIES, MPI-BGC, and UHEI from 3 intercomparisons.

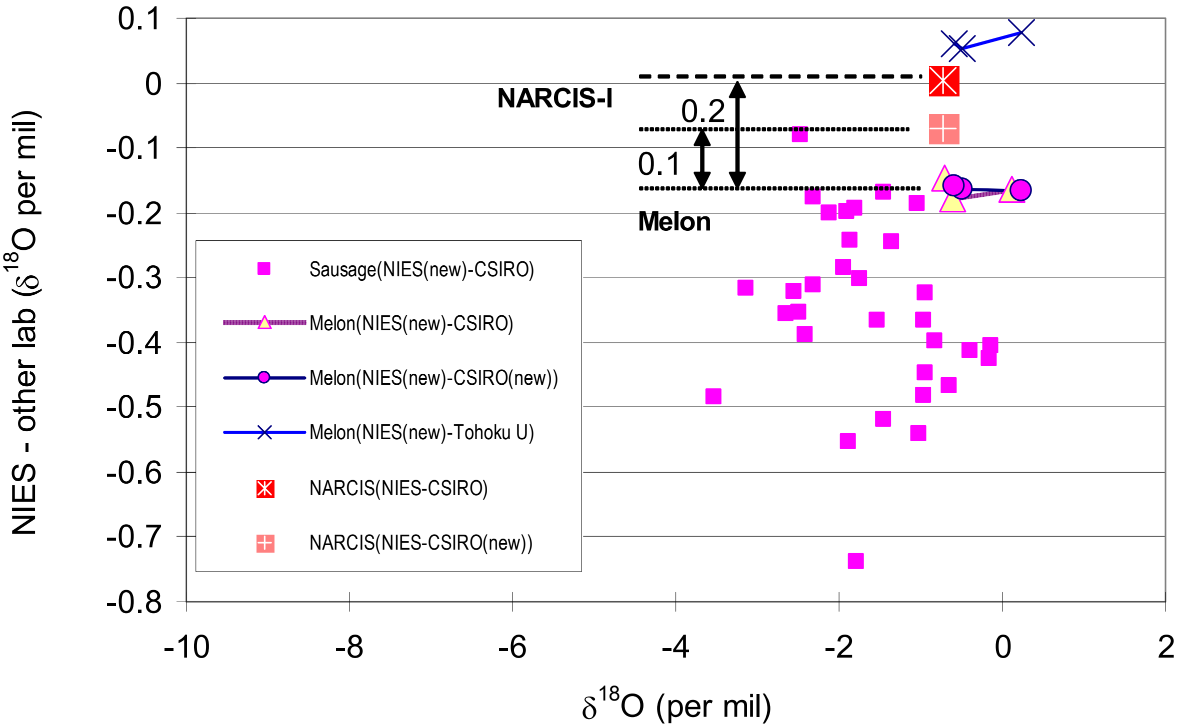

Figure 5: Observed δ^{18}O difference between NIES and CSIRO and Tohoku University from 3 inter-comparisons. The new “Melon” and NARCIS-I data comparison are also shown here. As a consequence of the CSIRO scale revision, differences in scale between air sample and pure CO$_2$ will become smaller by applying the new scale.

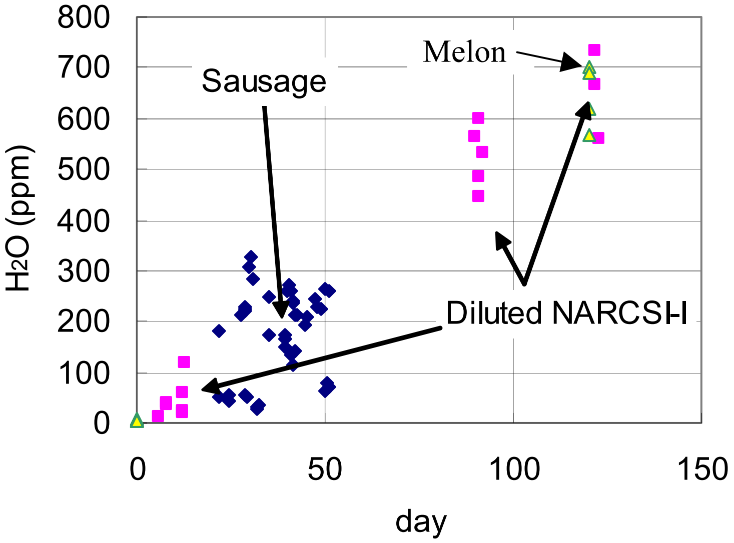

Figure 6: **Increase in water concentration in the 1 L glass flasks with storage time.**

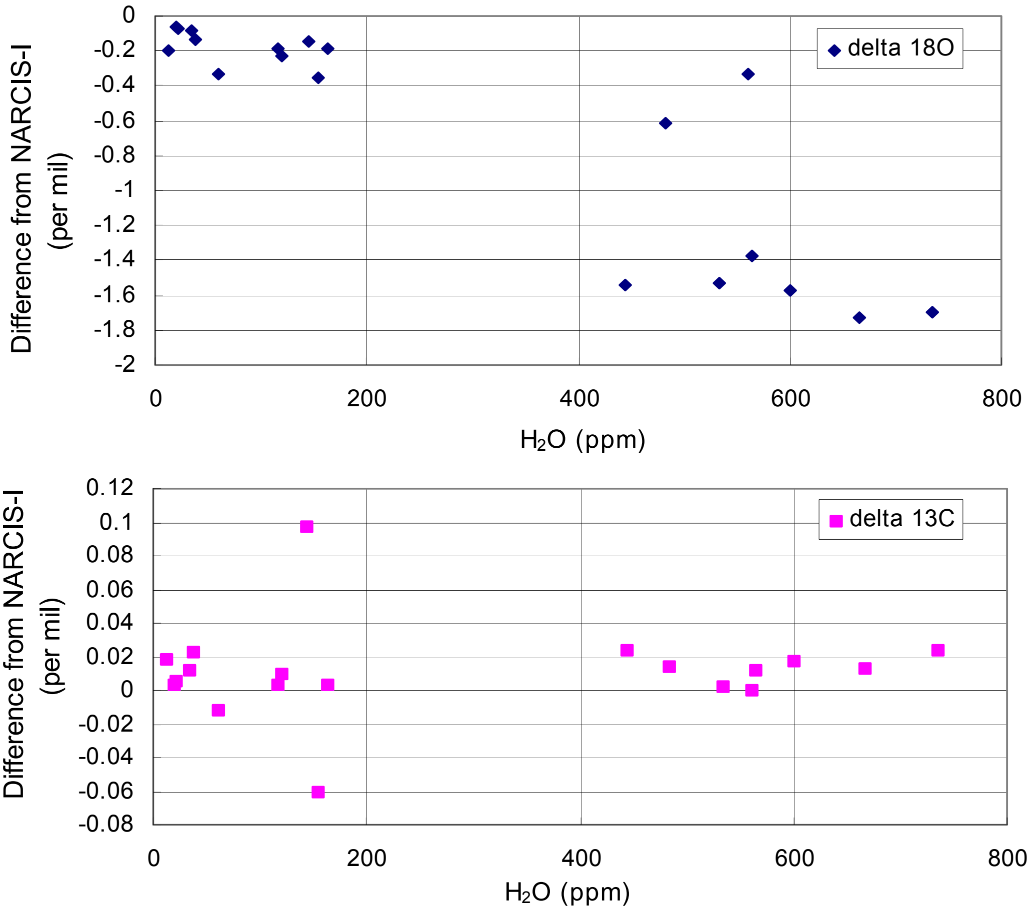

Figure 7: **Change in isotopic composition ($\delta^{13}C$ and $\delta^{18}O$) of the CO_2 in the 1 l flasks as a function of water content. The sample was NARCIS-I diluted into a 1L glass flask. Two samples showing large differences in $\delta^{13}C$ should be treated with caution as problems were observed during the dilution process.**

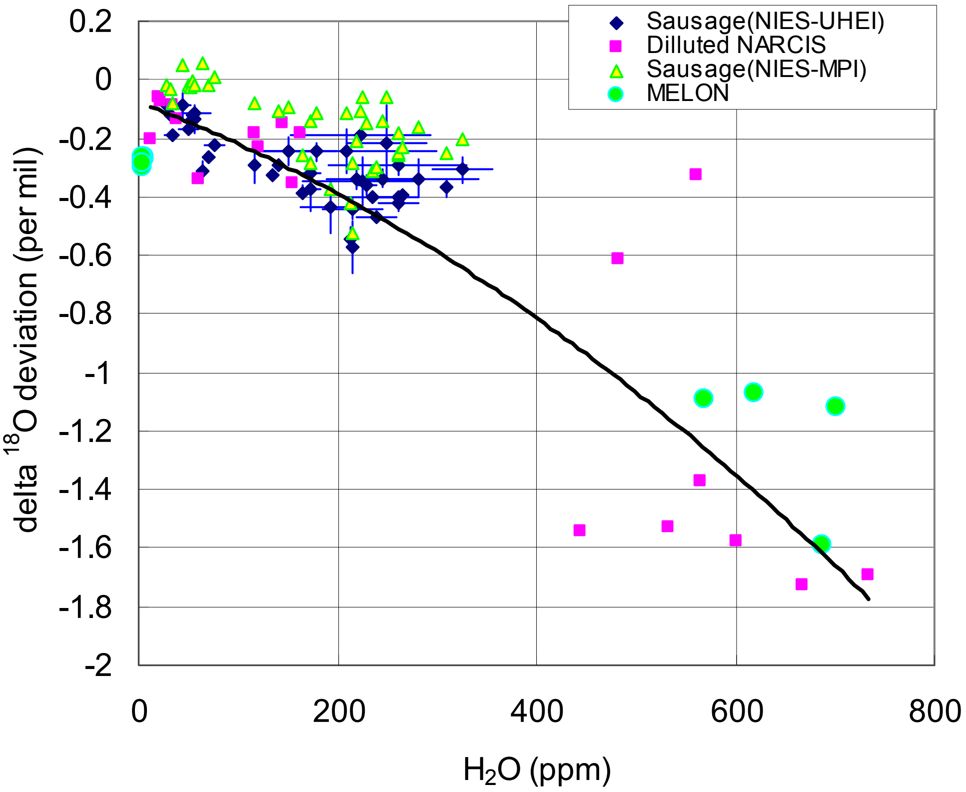

Figure 8: **Change in oxygen isotope ratio (δ^{18}O) with increasing water concentration from several experiments. The "Melon" samples were decanted from 4 "Melons" each into four 1L-glass flasks and kept in the laboratory for 120 day.**

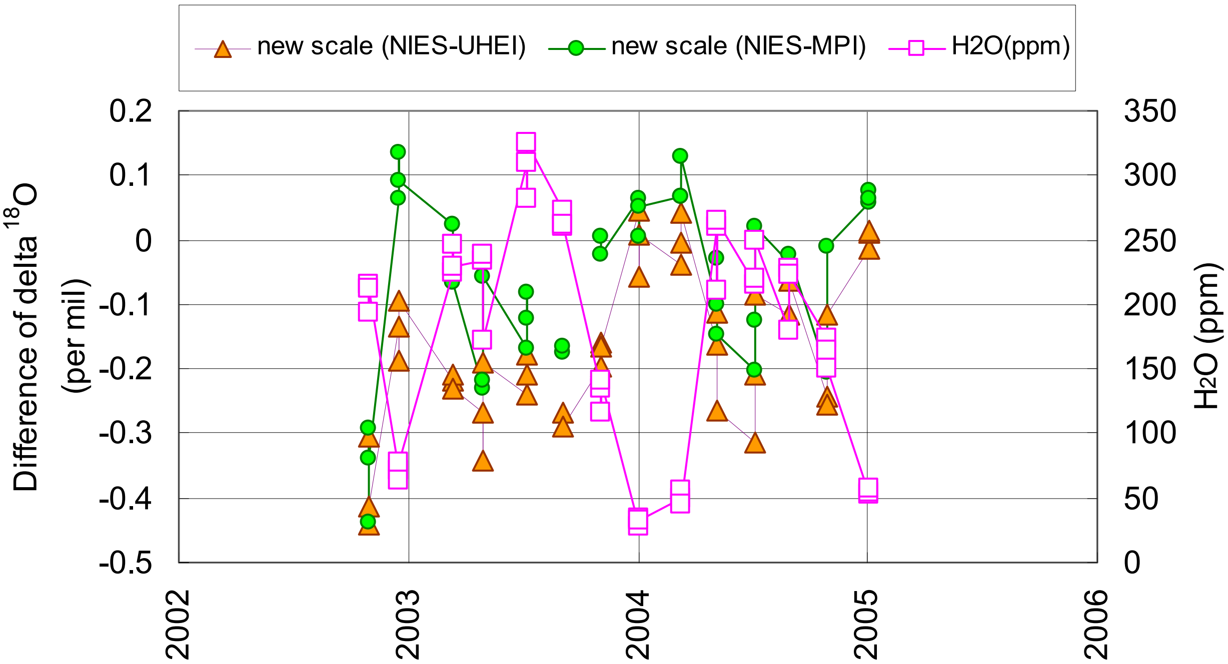

Figure 9: **Time series of water concentration and difference of oxygen isotope ratio in Sausage sample.**

1.6 Preparation of a Large Amount of Standard Air for Atmospheric O_2/N_2 Measurements

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1.6.1 Introduction

We have developed a continuous measurement system for the atmospheric O_2/N_2 ratio using a fuel cell analyzer (Sable Systems Co. "OXZILLA"), with a precision of ±2.4 per meg being comparable to those for previously established systems (e.g. Battle et al., 2005; Manning et al., 2005; Stephens et al., 2006). Our measurement system requires that each whole air standard is introduced into the analyzer every 24 minutes at a rate of 80 ml min^{-1} for 6 minutes for its calibration. Therefore the standard air is consumed in larger quantities when compared to a grab sampling method. To measure the atmospheric O_2/N_2 ratio continuously by operating our system, we need to prepare a large amount of standard air satisfying the following requirements: standard air should be filled in a large volume high-pressure cylinder, and the O_2/N_2 ratio and CO_2 mixing ratio of the standard air should be close to the present atmospheric values. For this purpose, we developed a new technique to produce standard air with different O_2/N_2 ratios and CO_2 mixing ratios in quantity, in cooperation with Taiyo Nippon Sanso Corp., Japan. A brief outline of the technique is given here.

1.6.2 Experimental Procedures

Industrially purified natural air was compressed in five 500 L high-pressure steel tanks at about 2.0 $x10^7$ Pa to use as a main ingredient of the standard air. The dew point of the purified air was measured to be below -80 °C. The total amount of purified air compressed in the tanks is enough to fill fifteen 48 L high-pressure aluminium cylinders at $1.4x10^7$ Pa (25°C), which is a task that we can accomplish in a day. As mentioned below, the O_2/N_2 ratios of the industrially purified air are lower by 1000 per meg or more than those of natural air. In order to adjust the O_2/N_2 ratio of the purified air to our demands, a proper amount of O_2 (N_2 when the O_2/N_2 ratio is too high) was first introduced into an evacuated high-pressure tank using a 0.5 L syringe, and then the purified air was added to 1.4 $x10^7$ Pa from the 500 L tanks through a manifold connecting them.

The amount of O_2 to be introduced can be calculated on the basis of the O_2/N_2 ratio of the purified air in the 500 L tanks. However, the O_2/N_2 ratios for the respective tanks are thought to be different. Therefore, the O_2/N_2 ratio of purified air from each 500 L tank was determined by analyzing air samples transferred into 0.55 L glass flasks from the relevant tank in several hours after filling it with the air, using a mass spectrometer (Ishidoya et al., 2003). We made such analyses three times to examine if the differences among the tanks depended on season. The results are shown in Figure 1. The average values of the O_2/N_2 ratios determined for the tanks were -1724±9, -1346±26, and -1227±6 per meg for April 8, June 26 and November 28, 2005, respectively. These averages are different by several hundred per meg, but the O_2/N_2 ratios for the five tanks in the same day are close to each other within 26 per meg. Considering these results, we decided to employ the average of the O_2/N_2 ratios of the purified air measured after being filled in the five 500 L tanks for the calculation of the O_2 amount.

In our mass spectrometric analysis of the atmospheric O_2/N_2 ratio, CO_2 in the sample affects its measured value, due to CO with mass 29 which is produced from CO_2 in the ion source of the mass spectrometer (Bender et al., 1994). Since the fuel cell analyzer measures the partial O_2 pressure relative to the whole air, the atmospheric O_2/N_2 ratio obtained from our continuous measurement system is also affected by the CO_2 mixing ratio of the sample air due to the dilution effect (Keeling et al., 1998). To minimize the correction for these effects, we injected CO_2 into the high-pressure tank using the syringe before introducing O_2, so that the CO_2 mixing ratio of the standard air was nearly equal to those of natural air.

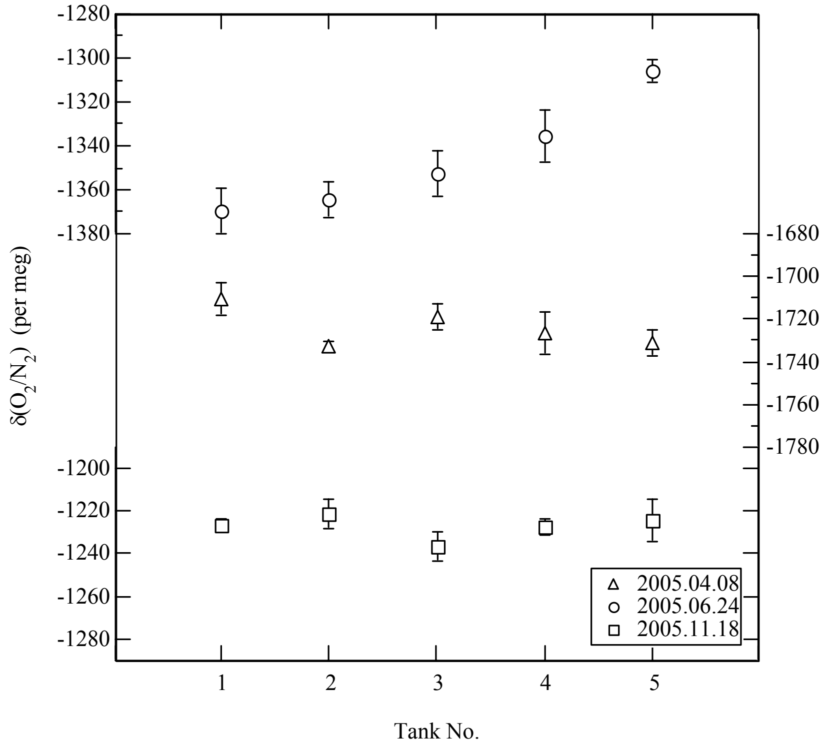

Figure 1: **O_2/N_2 ratios of the industrially purified air in several hours after being filled in five 500 L high-pressure steel tanks.**

1.6.3 O_2/N_2 Ratio of Prepared Standard Air

To validate the technique developed in this study, we prepared four 48 L standard air tanks with different values of O_2/N_2 ratio and CO_2 mixing ratio on June 26, 2005. The preparation of the standard air was made on the second day after filling the 500 L tanks with the industrially purified air. By collecting the air from the tank manifold just before preparing the standard air and analyzing it, we confirmed that its O_2/N_2 ratio was different only by 17 per meg from the average of the O_2/N_2 ratios determined for the 500 L tanks after the purified air was compressed. Our targets of the O_2/N_2 ratio and CO_2 mixing ratio for two of the standard air tanks were -400 per meg and 385 ppm, respectively, and the corresponding values for the remaining two air tanks were -100 per meg and 360 ppm. Based on the average O_2/N_2 ratio of -1346 per meg for the five 500 L tanks, the amounts of O_2 to be added to the 48 L high-pressure tanks were calculated to be 1.234 and 1.626 L (0°C) for attaining the respective target O_2/N_2 ratios of -400 and -100 per meg. The amounts of CO_2 were estimated to be 2.244 and 2.391L (0°C) for 360 and 385 ppm, respectively. In order to examine whether inside surface conditions of the high-pressure tanks affect the O_2/N_2 ratio and CO_2 mixing ratio of the standard air, we adopted two kinds of tanks with electro-polished and non-polished surfaces.

The four 48 L standard air tanks prepared by the above procedures were analyzed using the mass spectrometer and a non-dispersive infrared analyzer for the O_2/N_2 ratio and CO_2 mixing ratio, respectively, to compare to the values assigned in advance for the respective factors. It is seen in Table 1 that the measured values of the O_2/N_2 ratio agree with their assigned values to within 19 per meg. The measured CO_2 mixing ratios were systematically lower than the assigned values by about 4.5 ppm, which is probably due to errors in temperature estimation of CO_2 filled in the 0.5 L syringe. Figure 2 shows temporal variations of the O_2/N_2 ratio for the four standard air tanks. As seen from this figure, the O_2/N_2 ratio was stable to within 10 per meg over 40 days since the tanks are positioned horizontally. From the results of subsequent analyses, we confirmed that none of the standard air prepared in this study showed any systematic change in the O_2/N_2 ratio over 270 days. We also found from Table 1 and Figure 2 that the different surface conditions of the tank, i.e. electro-polished or non-polished, did not affect the value of the O_2/N_2 ratio of the standard air filled and its temporal stability.

Table 1: **Measured and assigned values of the O_2/N_2 ratio and CO_2 mixing ratio for four standard air prepared in this study.**

Tank No.	CQB18727 Non-polished	CQB18728 Non-polished	CQB18729 Electro-polished	CQB18730 Electro-polished
$\delta(O_2/N_2)$				
measured	-105.9	-392.0	-114.4	-398.0
assigned	-96.0	-399.3	-95.5	-397.9
Δ	-9.9	7.3	-18.8	-0.1
CO_2 mixing ratio				
measured	358.12	379.80	356.80	379.13
assigned	360.9	384.4	361.6	384.7
Δ	-2.8	-4.6	-4.8	-5.6

Δ means differences between the measured and assigned values, and "Non-polished" and "Electro-polished" indicate the inner surface conditions of the tanks used.

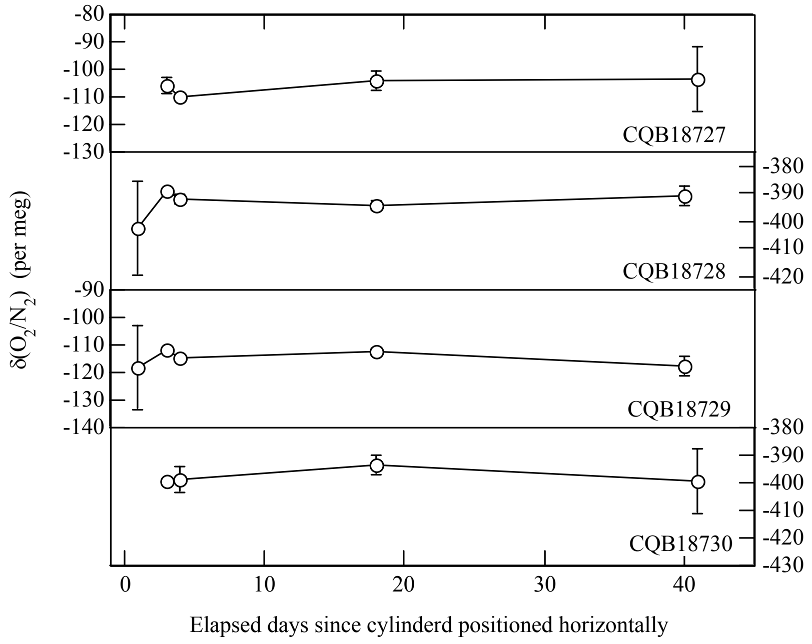

Figure 2: **Temporal changes in the O_2/N_2 ratios of four standard air prepared in this study.**

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1.7 Calibration of Atmospheric Hydrogen

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1.7.1 Introduction

Interest in atmospheric hydrogen has increased in recent years as scenarios for a future hydrogen fuel economy are proposed and discussed _(Prather, 2003). Such a development could cause a significant increase in the anthropogenic source strength of hydrogen. Rising levels of atmospheric hydrogen would consume hydroxyl radicals and thus decrease the oxidation capacity of the atmosphere. This would in turn influence the budget of the greenhouse gases such as methane ("indirect greenhouse gas effect") (IPCC, 2001). In addition, a significant increase in the stratospheric H_2 load would lead to increasing levels of stratospheric water vapour, which is essential for the energy balance and the ozone budget of the stratosphere. According to global budget estimates sources and sinks of H_2 are approximately balanced, but there remain large uncertainties. These uncertainties are at least in part due to inconsistent information from different data sets. The two studies with the longest atmospheric monitoring records of hydrogen mixing ratios have been published by Novelli et al. (1999) and Langenfelds et al. (2002). In these two studies different trends of H_2 mixing ratios were observed at the Cape Grim monitoring site in the 1990s. An intercomparison experiment conducted by the two groups showed an offset that was suspected to be due to different internal calibration scales used by each laboratory. In the absence of a common, internationally recognized scale for H_2, multiple scales have been listed in the literature. The lack of knowledge of the conversion factors of these scales has been identified repeatedly as a major contributor to difficulties in comparing different data sets (Masarie *et al.*, 2001; Schmidt and Wetter, 2002; Simmonds *et al.*, 2000).

1.7.2 Reference Gas Stability

A major problem that has inhibited the setup of a hydrogen scale is the non-stability of H_2 reference gases. Commonly used containers for trace gas reference standards are aluminium cylinders but it appears that most of these tanks are not suitable for H_2 standards. They tend to produce H_2 over time and hence lead to significant concentration changes. The H_2 concentration trend of five such standard gases monitored at MPI-BGC is depicted in Figure 1. Alternative containers that have successfully been tested for H_2 in air storage are internally electro-polished stainless steel canisters.

The H_2 scale at the MPI-BGC has been linked to the H_2 calibration scale set up by CSIRO (Francey *et al.*, 1993) through a reference gas purchased in 2002. The response of the Reduction Gas Analyser (RGA 3, Trace Analytical) was characterized making a dilution series and determining the dilution factor analysing CH_4 mixing ratios on a GC-FID. H_2 mixing ratios were assigned to four air mixtures stored in two stainless steel 40 L, one 50 L steel and one 50 L aluminium cylinder, respectively. In 2004, three additional 34 L stainless steel cylinders (Essex Cryogenics) were purchased and filled with standard gas at different levels (450-650 ppb). This extended set of reference gases is now being used as calibration scale (MPI2004 scale). The stability of the scale has been checked by different approaches:

- The residuals of the regression fit of the calibration curve (shown in Figure 2) are indicative of a consistent behaviour of the whole calibration set. However, it is not possible to exclude a uniform drift of all standard gases (as shown for the Luxfer gases in Figure 1) by this way.
- Reference gases were stored in glass flasks of 5 L volume equipped with a single PCTFE sealed valve. Repeated reanalysis did not show any drift relative to the calibration suite within one year. However, the limited number of analysis possible with the given amount of sample gas restricts the statistical value of the results.
- An ongoing intercomparison exercise has been started with CSIRO in 2002 based on shared flask samples as well as different sets of flasks filled with the same sample. There is good agreement in the H_2 results and no trend has become evident.

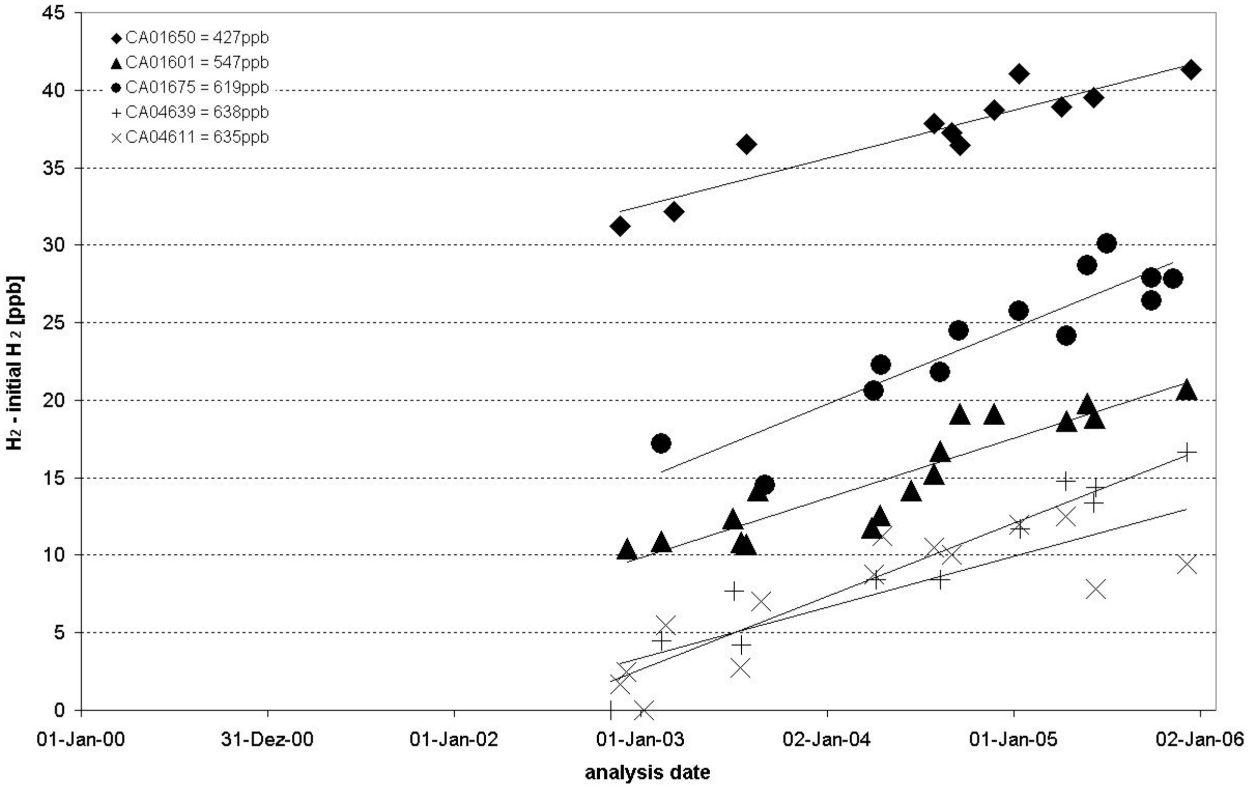

Figure 1: Trend of hydrogen mixing ratios in reference gases. Values displayed by black symbols represent gases in 29 L Luxfer cylinders filled by CSIRO. Initial H_2 values have been analysed by CSIRO in beginning of 2000. Values displayed by crosses show the trends of reference gases provided by CMDL. Initial H_2 values were determined at MPI-BGC.

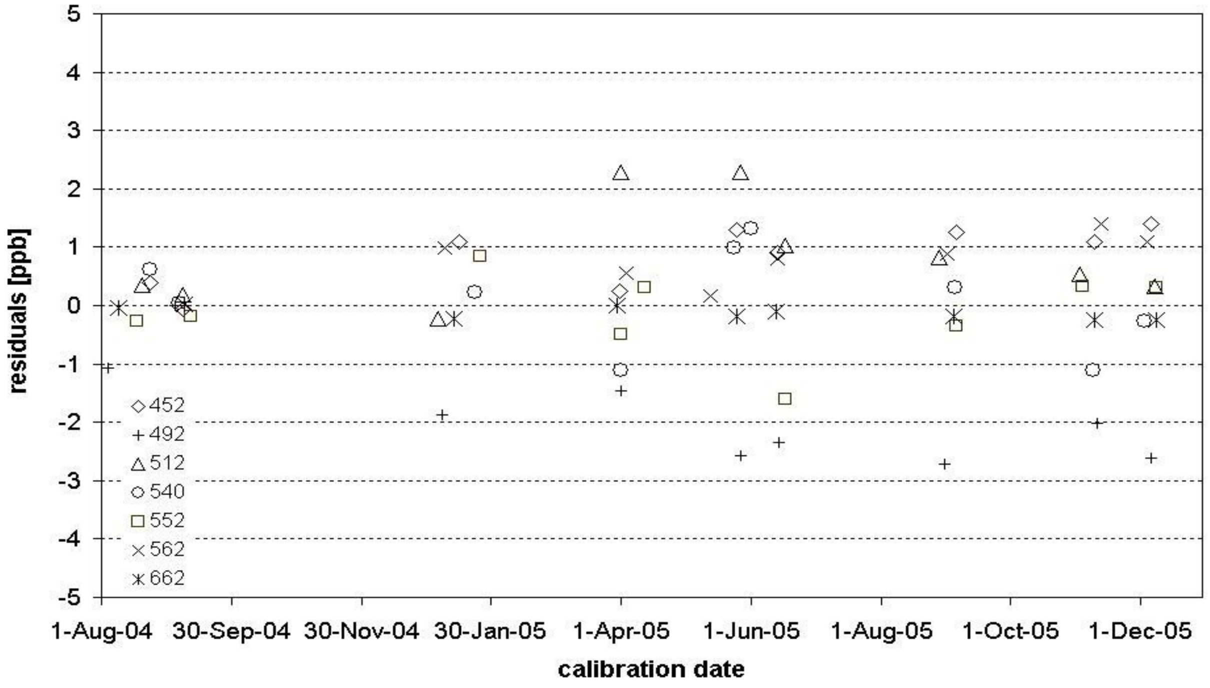

Figure 2: Calibration residuals of the MPI2004 scale; symbols refer to individual standard gas cylinders identified by mixing ratio in legend.

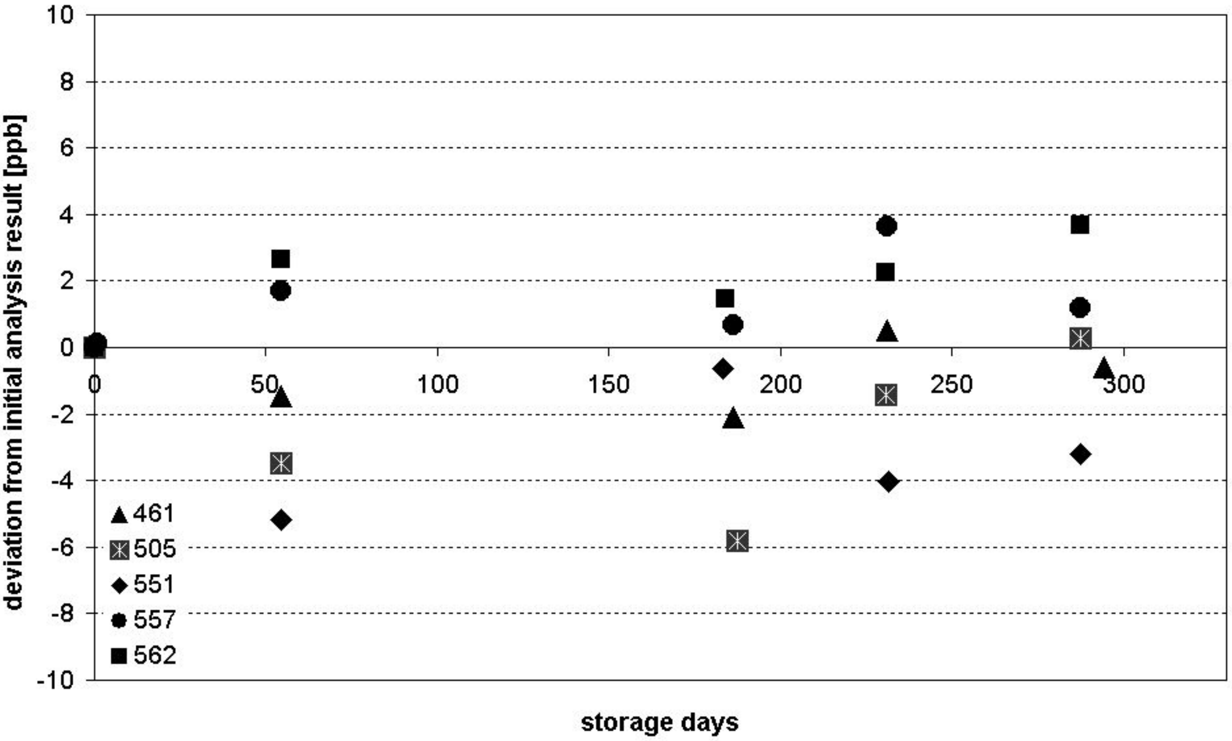

Figure 3: Storage test of H_2 reference gases in 5 L glass flasks; symbols refer to individual standard gas cylinders identified by mixing ratio in legend.

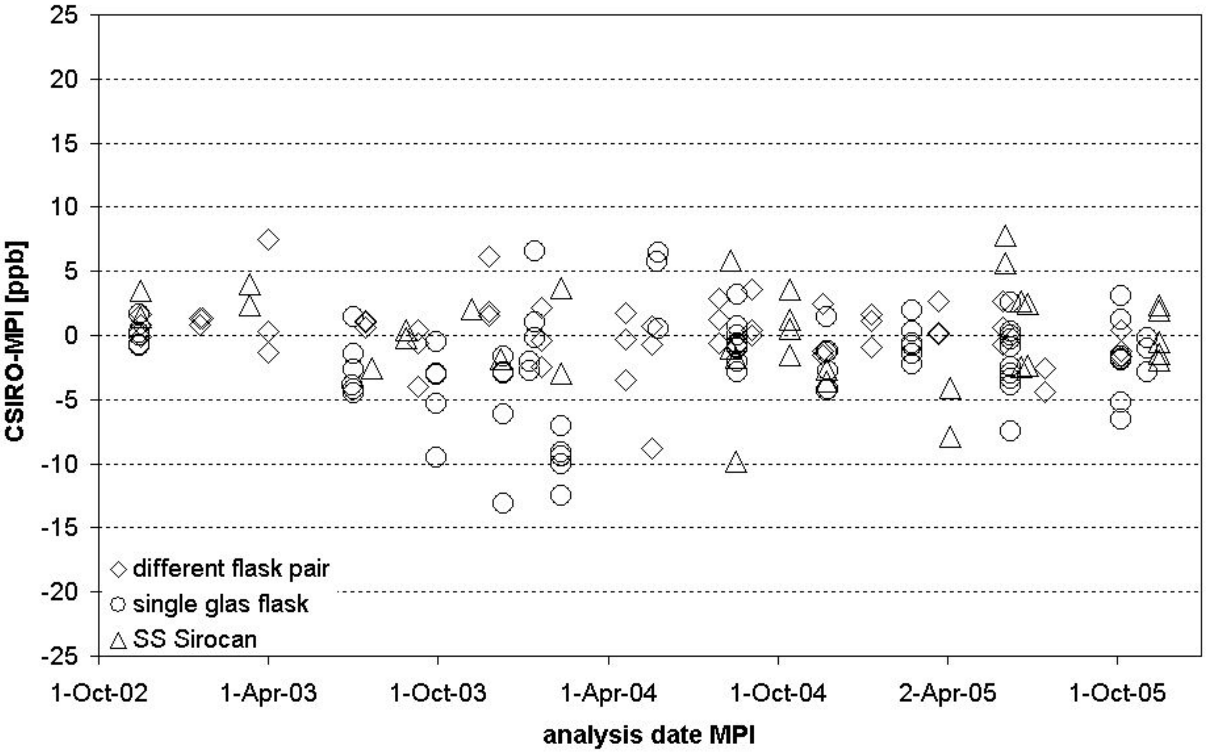

Figure 4: Intercomparison Results with CSIRO. Diamonds represent the deviation of the flask pair means of independent sets filled with the same air; circles show the deviation in H_2 results of single shared glass flask samples; triangles represent the deviation in single shared flask samples (stainless steel, 1.6 L).

1.7.3 One-Step Dilution of New Standards

While all of these tests may exclude major scale drifts none of them has the ability to exclude a small drift over a longer time range. To provide a check for such potential drifts a new method to regularly prepare reference gas mixtures by a one step dilution has been established. The procedure consists of the following steps:

H_2 is filled in a sample loop (250-400 µL). After sufficient flushing the hydrogen source is disconnected and the ambient pressure and temperature of the sample loop are measured. By switching the valve the sample loop contents are isolated. The valve is then connected to a high pressure cylinder filled with a diluent gas and an evacuated 6 L aluminium cylinder that is placed on a precision balance (see Figure 5). The inter-connecting stainless steel lines are evacuated and flushed with the diluent gas (nitrogen for most experiments) that is flowing through a restrictor capillary and a purifying cartridge. The valve is then switched to put the sample loop in line and the hydrogen is transferred to the mixing cylinder at a flow rate of ca. 3L/min. After filling the dilution cylinder with the required amount of diluent gas (380 µL of hydrogen in 700 L of diluent for a 540 ppb mixture) the transfer tubing is disconnected. The cylinder mass is weighed and the amount of diluent calculated using the molar masses $n_{Nitrogen}$ = m / 28.013 g/mol or n_{air} = m / 28.974 g/mol (Francey *et al.*, 1993).

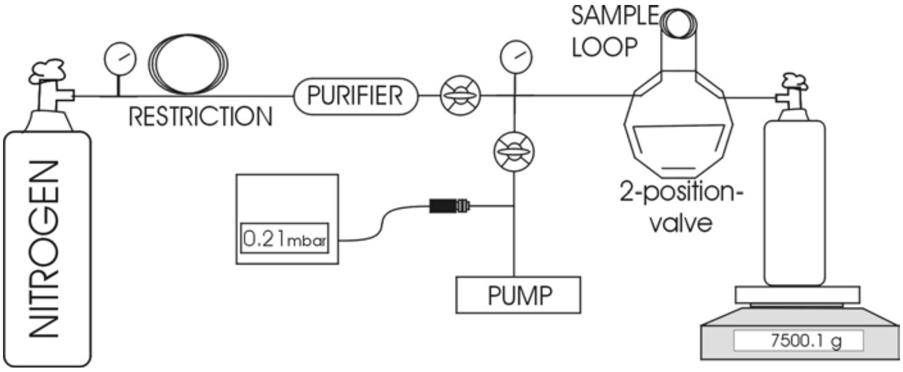

Figure 5: **Set-up of the one-step dilution system.**

The gas mixture is analysed after a few hours. All samples were analysed in numerous replicates (8-30) in order to get a standard error of below 1 ppb (< 0.2 %). The results presented in Figure are expressed as deviation of the analytical result based on the MPI2004 scale minus the value expected from the mixing experiment. The scatter of the results is on the order of the analytical noise demonstrating a reproducibility of the mixing experiment of ≤ 0.2 %. One single result that showed a larger deviation exceeded the calibrated range (690 ppb). It should be noted that there is a consistent offset of 14.5 ppb between the results of the dilution experiment and the MPI2004 H_2 scale.

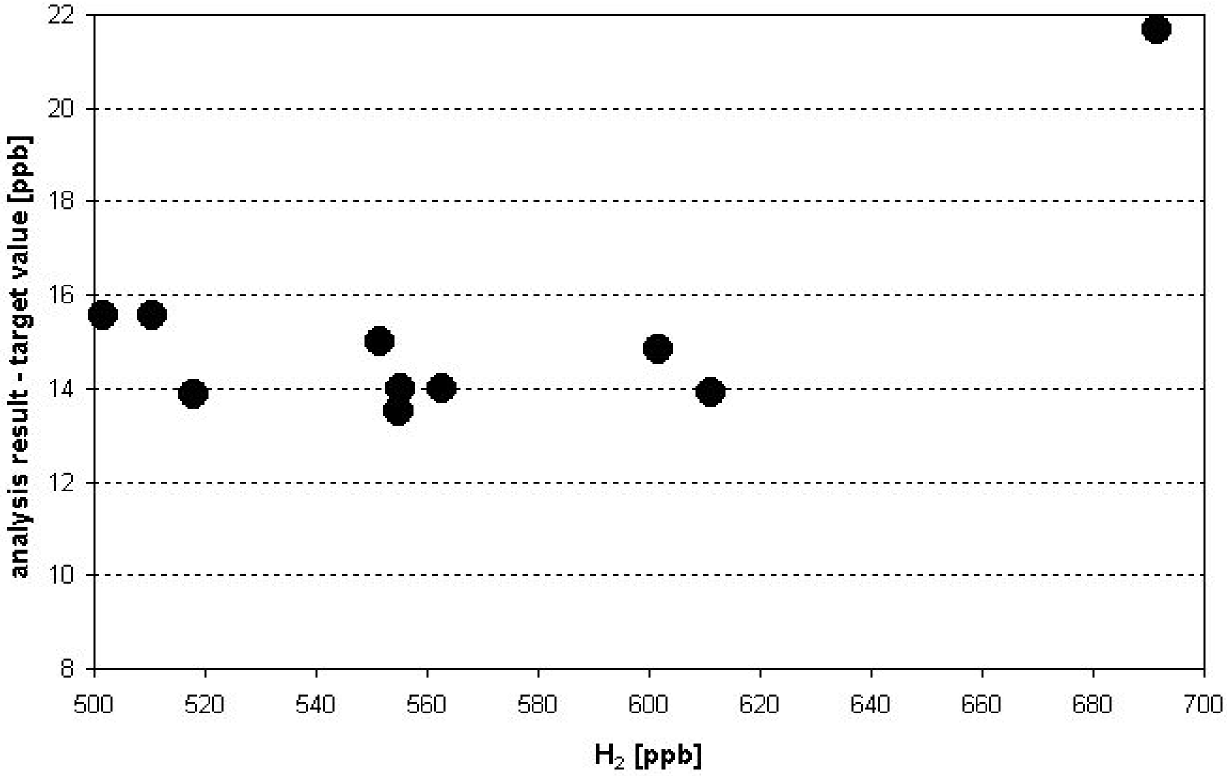

Figure 6: **Result of repeated dilution experiments. (Sample loop volume = 380 µl, diluent = N_2, Valcon E valve rotor. Hydrogen mixing ratios are quantified based on the MPI2004 scale).**

1.7.4 Discussion

To assess the uncertainty and possible errors of the method the following limiting factors were taken into consideration:

1. Purity of hydrogen and non-ideal behaviour of hydrogen gas.
2. Accuracy of sensors (temperature, pressure) and balances.
3. Volume uncertainty of the sample loop.
4. Purity of diluent.
5. Loss or production of H_2 at surfaces within the dilution assembly.

1. The electrolytically generated hydrogen is purified using a Palladium diffusion cell. A purity of >99.9999% according to the H_2 generator's specification (Parker Whatman 75-32) is assumed. The deviation from the ideal gas law is taken into account using the second virial coefficient B = 15 cm^3/mol (^{Kehiaian}, 1997). The associated correction of 0.06 % is small and any uncertainties associated with the coefficient are estimated to be negligible.

2. The calibration of the PT1000 temperature (GTF175, Greising electronic) sensor was verified with a well calibrated high-precision thermometer (DP251, Omega) and proven to be accurate within its 0.1°C resolution. In contrast, a check of the pressure sensor (DI2000, Leybold) with a high precision pressure sensor (Baratron, MKS) revealed an offset of 1.6 mbar at 980-1000 mbar that had to be accounted for. All utilized balances are surveyed by the German calibration service annually. The uncertainties associated with the balances used for sample loop volume determination and weighing of the transferred mass of diluent gas are 0.05 mg (AT261, Mettler-Toledo) and 0.2 g (CP8201-0CE, Sartorius), respectively.

3. Each of the three sample loops was filled with degassed, high purity water and weighed. This resulted in standard errors of 0.05 mg equal to the balance accuracy and results in relative errors that are much smaller than the analytical precision (< 0.03%). The gravimetric determination of the sample loop volumes was made in the same temperature range as the dilution experiments (295-296 K). The respective sample loop volumes were calculated using the temperature dependent density of water (0.9977 mg/µl at 22.4 °C (CRC, 1997)) correcting for the mass of the displaced air. The total volume filled with hydrogen is increased by 2.46 µL resulting from the internal volume of the employed valve (Kurrmann, 2005). Most experiments were performed using a 380 µL sample loop. There was no significant offset in the results using two different loops (245µL and 345µL).

4. A blank determination of the diluent gases did not result in a rigorous purity assessment because of a non-sufficient detection limit of the analytical method of 15 ppb. Further purification has therefore been made. Nitrogen was passed through an Aeronex 70KFI4R cartridge (Mykrolis) that can tolerate pressures up to 200 bar and that is specified to reduce H_2 residues to below 1 ppb. Air is purified using a 500 mL cartridge filled with 434 g of Sofnocat 514 (Molecular Products) followed by a drying cartridge filled with magnesium perchlorate. Special care was taken that the flow rate of the gas transfer was restricted to $\approx$ 3 L/min *i.e.* within the operative range of the respective cartridge. Most dilution experiments have been made using nitrogen. The use of purified air as diluent resulted in mixing ratios that were significantly higher by about 3 ppb. This might indicate an insufficient purification of the diluent air and further tests will have to be made.

5. It is essential for the method to exclude any loss of H_2 or contamination with excess H_2 during any of the steps of the experiment. The only polymer part that is in contact with the H_2 is the rotor of the Valco two position valve. It is conceivable that some hydrogen might diffuse into the polymer either during the filling of the sample loop or while the sample loop is isolated between filling and transfer. However, the time while the sample loop is isolated is relatively short (< 5 min.) compared to the time of transfer when hydrogen-free nitrogen (or air) is flowing over the polymer surface (ca 120 min.). Therefore, any H_2 adsorbed on the polymer surface should back-diffuse and would not alter the mixing ratio. By contrast, if some H_2 would adsorb on the polymer during then loop filling process this could result in some excess hydrogen. In order to check this possibility two dilution experiments were made with a second valve equipped with an alternative Valcon M rotor that is made especially for impermeability for light gases. No significant difference in the average results appeared indicating no major effect. As pointed out earlier, most Luxfer aluminium cylinders have been found to produce hydrogen. This makes them unsuitable containers for long-term storage of reference gases. However, in the case of the dilution experiment the requirement for stable hydrogen mixing ratios extends only for the time of the experiment including analysis (1-3 days) and thus any growth rate < 0.5 ppb/d can be tolerated. Figure 7 shows that the H_2 concentration trend of an air sample in the cylinder used in this study is clearly meeting this requirement (drift $\approx$ 0.07 ppb/d at 50 bar). Yet, there have been other, newly purchased cylinders of the same type that exhibited large H_2 growth rates of up to 250 ppb/d at 3 bar filling pressure which would bias the experimental result by 10 ppb/d (at an experimental pressure of 120 bar).

1.7.5 Summary

In order to improve atmospheric H_2 data there is urgent need to improve the calibration of H_2 measurements. Intercomparison exercises are crucial for evaluating the comparability of data. Special attention has to be paid to the containers for H_2 reference gases. The one step dilution method presented in this study provides a means to check the stability of a H_2 calibration scale. None of the discussed limiting factors appears to affect the method precision to more than 0.1 % resulting in a cumulative uncertainty that is well below the analytical precision of a reduction gas analyser.

This also makes it a promising approach to improve absolute hydrogen calibrations and it gives strong evidence that the MPI2004 H_2 scale has to be corrected by 14.5 ppb.

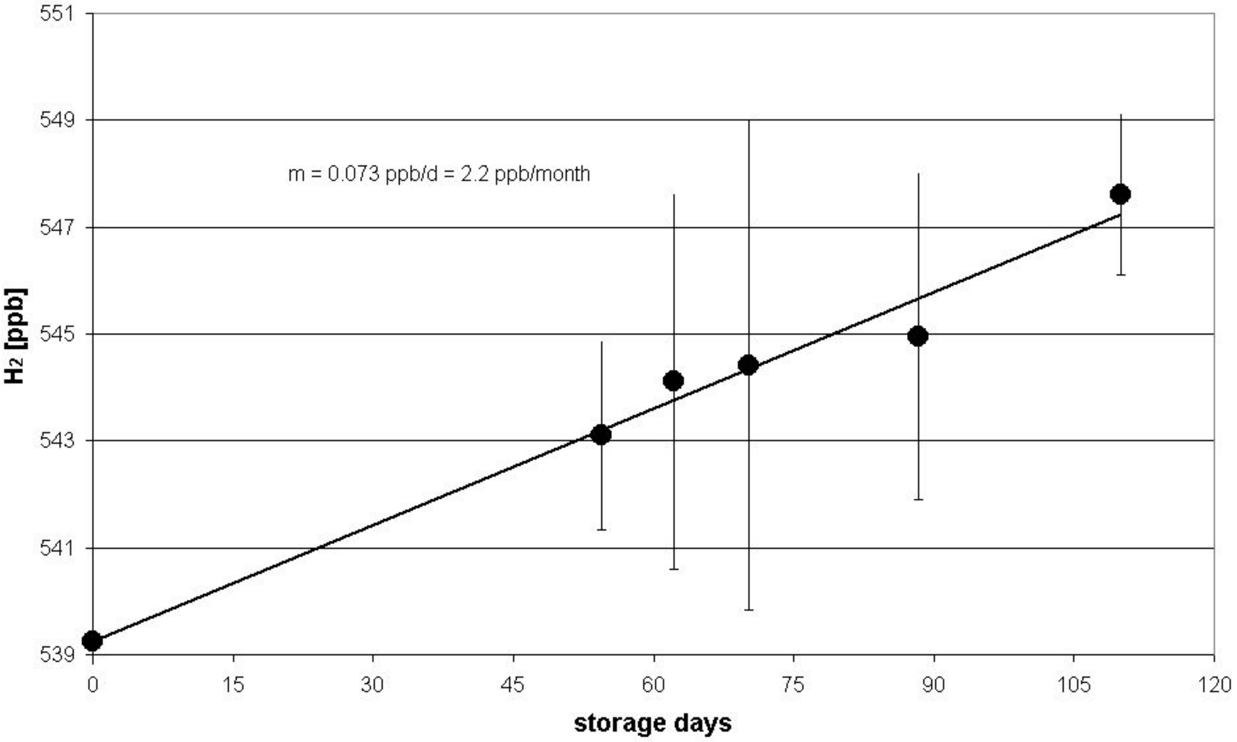

Figure 7: Hydrogen growth in dry air in 6 L Luxfer cylinder FA01375 (50 bar).

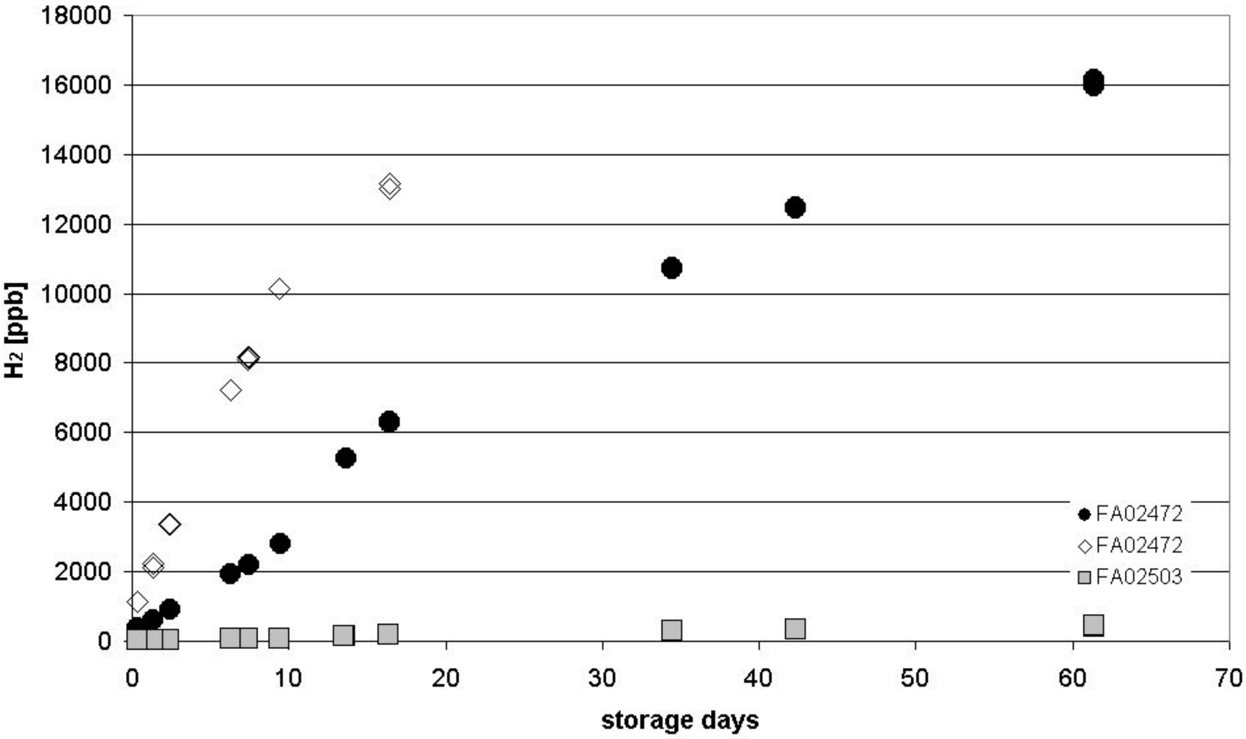

Figure 8: Hydrogen growth in synthetic air in three new 6 L Luxfer cylinders (2 bar).

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2. DATA QUALITY AND DATABASES

2.1 Quality Assurance and Quality Control of CO and CH_4 Measurements in GAW

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GAW QA/SAC Switzerland and WCC-Empa, Dübendorf

2.1.1 GAW QA/QC Principles

One of the Global Atmosphere Watch programme's major contributions to atmospheric sciences is a relatively stringent framework for quality assurance/quality control of the participating stations. Although difficult to enforce in a voluntary programme, it defines a baseline for what is considered acceptable. The main principles of the GAW QA/QC system for each measurement parameter involve (*Figure 1*) (*WMO*, 2001):

- Use of only one single reference standard.
- Shortest traceability chain possible.
- Use of harmonized measurement techniques.
- Instrument operation according to SOPs or Measurement Guidelines.
- Regular system and performance audits.
- Proper documentation of operations at stations.
- Adoption and use of internationally accepted methods and vocabulary concerning uncertainty assessment.
- Adequate training of operators.

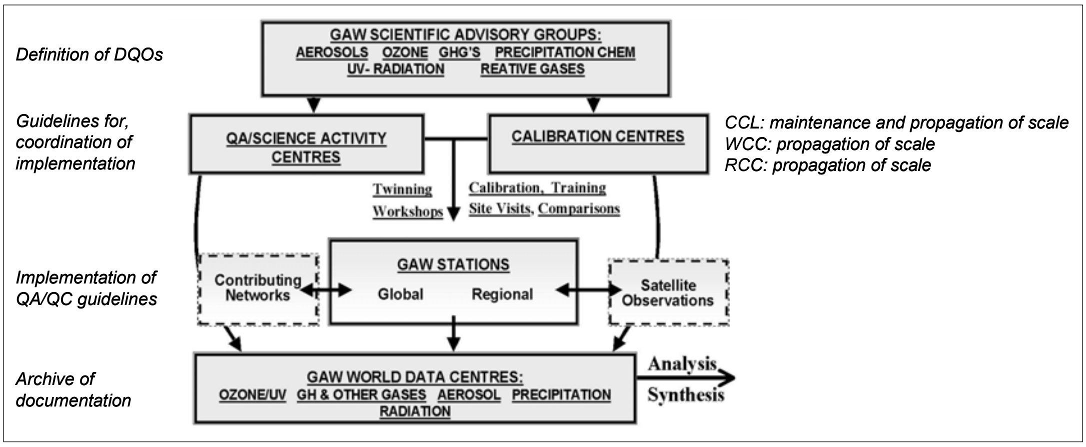

Figure 1: Role of the various partners in GAW with respect to QA/QC.

2.1.2 Implementation for CO and CH_4 (in situ) Measurements

2.1.2.1 Reference Standard

NOAA/ESRL's Global Monitoring Division (formerly CMDL) of the National Oceanic and Atmospheric Administration (NOAA) acts as the Central Calibration Laboratory (CCL) by hosting the WMO GAW Reference Standards for carbon monoxide (CO) and methane (CH_4). They maintain a set of primary and secondary standards and produce laboratory standards that propagate the scale to the GAW World Calibration Centre (WCC) and to individual monitoring sites world-wide on a cost-recovering basis.

2.1.2.2 Traceability Chain

If stations have acquired their standards in sufficient numbers directly from GMD, the traceability chain is directly from the stations to the CCL. In many cases, however, even GAW stations obtain their standards from somewhere else, or have obtained an insufficient number of cylinders from the CCL, or their cylinders have never been returned to the CCL for re-calibration. In these cases, the WCC for Surface Ozone, Carbon Monoxide and Methane (WCC-Empa), hosted by the Swiss Federal Laboratories for Materials Testing and Research (Empa), is the only official link that provides traceability of the station to the GAW reference standard. In all cases, the regular inter-comparison of Global GAW stations by WCC-Empa is a very valuable independent assessment of the calibration of stations.

2.1.2.3 Harmonized Measurement Technique

The objective to generate globally harmonized data sets calls for harmonized measurement techniques. While this may not be a theoretically well-founded requirement, experience shows that various analytical techniques, or even different instruments, can give different results. Within GAW, the techniques that are currently in use comprise of:

- For CO: NDIR, RGA, cat/GC-FID, VUV fluorescence.
- For CH_4: GC-FID.

The Scientific Advisory Group for Reactive Gases is currently in the process of evaluating the techniques for CO measurements and to make recommendations concerning the trade off between instrument precision, linearity, and cost. It is likely that for CO, cat/GC-FID will become more important, RGA less important, and FTIR be included as the technique for total column.

2.1.2.4 SOPs or Measurement Guidelines

These are almost finished for CH_4 and in progress for CO.

2.1.2.5 Regular system and performance audits

For GAW stations, QA/SAC Switzerland and WCC-Empa conduct regular system and performance audits every three to four years. For Regional and Contributing stations, a system of auditing still needs to be implemented.

2.1.2.6 Documentation at Stations

According to the GAW QA/QC principles, log-books are a cornerstone of all monitoring activities. The adequacy of log-books is checked during station audits.

2.1.2.7 Uncertainty Assessment

It is commonly accepted that a measurement is incomplete without a statement of its uncertainty. The GAW Strategic Plan (*WMO*, 2001) references the relevant ISO documents (ISO, 1993a; 1993b, 1995) that are recommended for adoption by the GAW community for estimating and communicating uncertainties. This has been documented for surface ozone (Klausen*, et al.*, 2003), but the approach is also valid for other trace gases.

2.1.2.8 Training

As part of a general effort of capacity building, GAW strongly supports operator training. One-on-one training is provided during station audits by WCC-Empa, in the form of training courses by the GAW Training and Education Centre (GAWTEC), and through exchange of scientists.

2.1.3 Carbon Monoxide

2.1.3.1 Travelling Standards

Aluminium cylinders (2-6 L) are filled with ambient air to 100 bar. During filling, the CO mole fractions are adjusted to cover the entire ambient range by either adding CO from a 50 ppm (synthetic air) cylinder, or by removing CO using Sofnocat™. The mole fractions in these cylinders are determined by calibration against NOAA/GMD laboratory standards using the HVUV fluorescence technique (Aerolaser™ instrument). The linearity of the AeroLaser™ instrument has been demonstrated repeatedly using a dilution unit with molbloc™ flow sensors and a 10 ppm CO cylinder. Due to the remaining inconsistencies in the NOAA/GMD CO scale (Klausen, 2006), only one cylinder (CA02854, 295.5 ppb, WMO-2000) is taken as the reference. The absolute accuracy and stability of cylinder CA02854 has been confirmed over recent years by inter-comparison with higher concentration standards obtained from various metrological institutes (Figure 2).

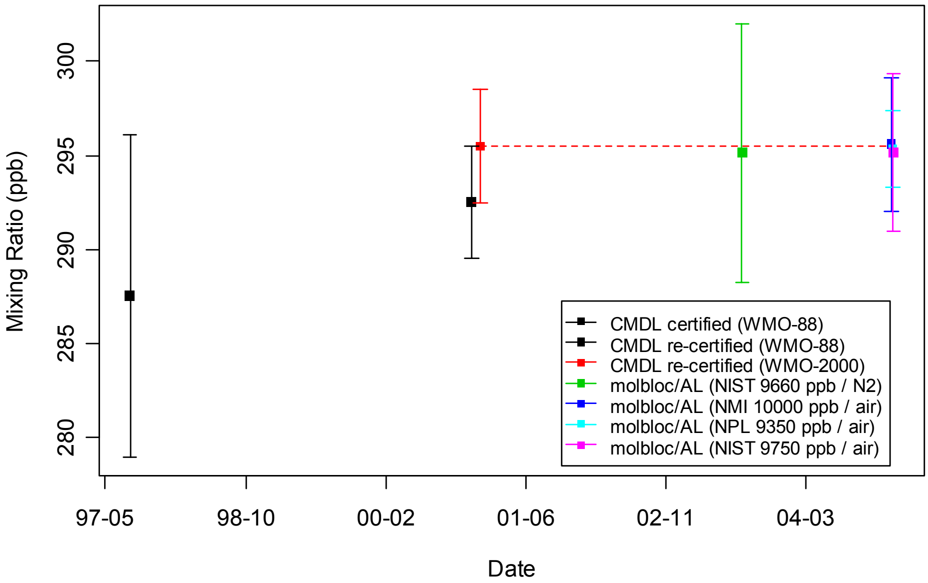

Figure 2: **Stability of CO in NOAA/GMD cylinder CA02854 maintained at WCC-Empa.**

2.1.3.2 Audit Results

Since 1997, 21 performance audits at 13 stations were conducted by WCC-Empa, using a suite of at least 5 travelling standards in each case. Comparing the mixing ratios obtained by the individual stations with those assigned by WCC-Empa with linear regression analysis, 12 audits yielded a regression slope greater than one, while 9 audits yielded slopes less than one. The almost equal count of positive and negative signs is taken as an indication that WCC is ‘somewhere in the middle’ and not likely to be biased. Overall, these audits did not indicate a great deal of consistency, even for a given station. As expected, NDIR instruments exhibited larger uncertainties than instrument based on mercuric oxide (HgO) reduction, however, the latter exhibited more systematic regression residuals (Figure 3). This confirms well-established suspicions concerning the non-linearity of instruments based on the mercuric oxide (HgO) reduction technique and highlights the need for a sufficient number of internally consistent calibration standards.

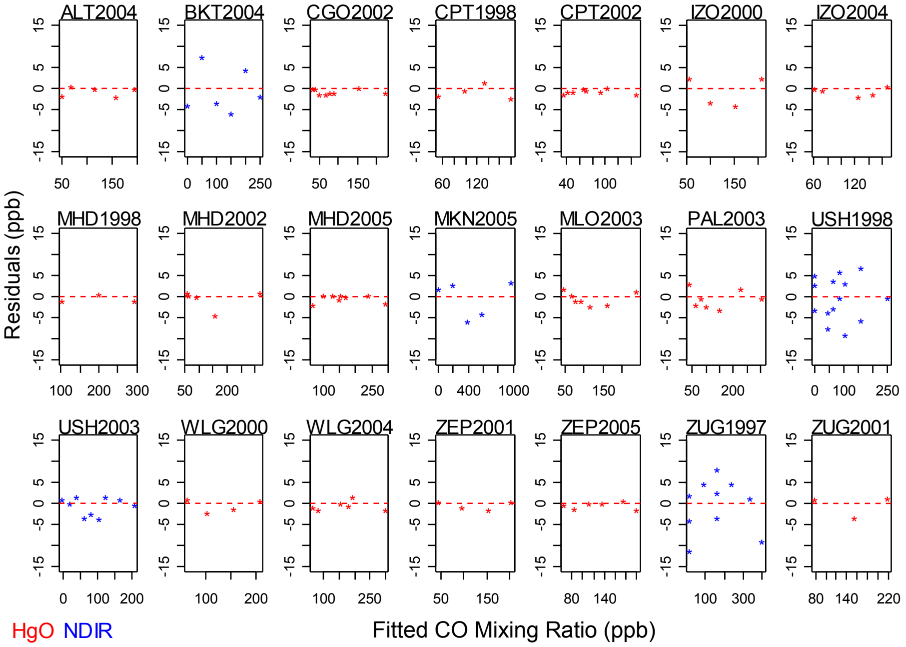

Figure 3: **Tukey-Anscombe plots of regression residuals for CO inter-comparisons. Titles of plots refer to site codes and years as follows: ZUG: Zugspitze; ZEP: Zeppelin Mountain, Ny Alesund; WLG: Mt. Waliguan; USH: Ushuaia; PAL: Pallas-Sodankyla; MLO: Mauna Loa Observatory; MKN: Mt. Kenya; MHD: Mace Head; IZO: Izana Observatory; CPT: Cape Point; CGO: Cape Grim Observatory; BKT: Bukit Koto Tabang, Indonesia; ALT: Alert.**

The result of calibration biases found during these audits is perhaps best illustrated by Figure 4. Based on a target accuracy of 5% maximum deviation between the station and WCC-Empa reference gas over the ambient concentration range at each individual site, the figure indicates non-compliance in the majority of cases.

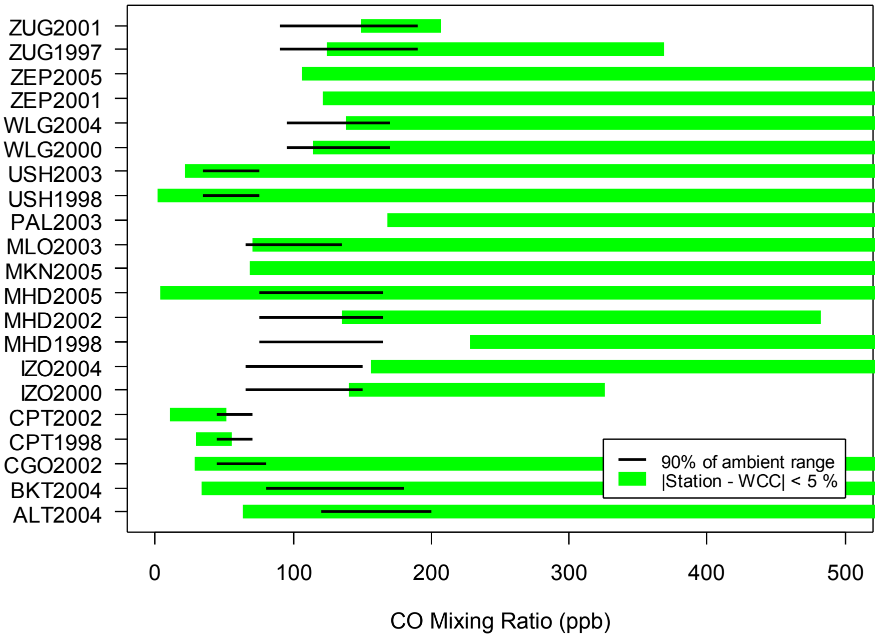

Figure 4: **Comparison of the ambient CO mole fraction range (90% inter-percentile range) (black lines) with the range of calibration gases not exceeding a threshold absolute deviation of 5% between station and WCC-Empa, based on linear regression analyses (green bars).**

2.1.4 Methane

2.1.4.1 Travelling Standards

Aluminium cylinders (2-6 L) are filled with ambient air to 100 bar. During filling, the CH_4 mole fractions are adjusted to cover the entire ambient range by either adding CH4 from a 50 ppm (synthetic air) cylinder, or by adding pure synthetic air. The mole fractions in these cylinders are determined by calibration against 3 NOAA/GMD laboratory standards using the GC-FID technique. The linearity of the FID was repeatedly demonstrated using a dilution unit with molbloc™ flow sensors and a 10 ppm CH4 cylinder.

2.1.4.2 Audit Results

Since 2001, 11 performance audits at 10 sites were conducted by WCC-Empa, using a suite of at least 5 travelling standards in each case. Comparing the mixing ratios obtained by the individual stations with those assigned by WCC-Empa with linear regression analysis, 7 audits yielded a positive sign of the regression slope, while 4 audits yielded a negative sign. The regression residuals (Figure 5) were generally unstructured, supporting the adequacy of a straight line regression model. For most sites, the residuals were within ±5 ppb, and for all sites, they were within ±10 ppb (order of 0.5%).

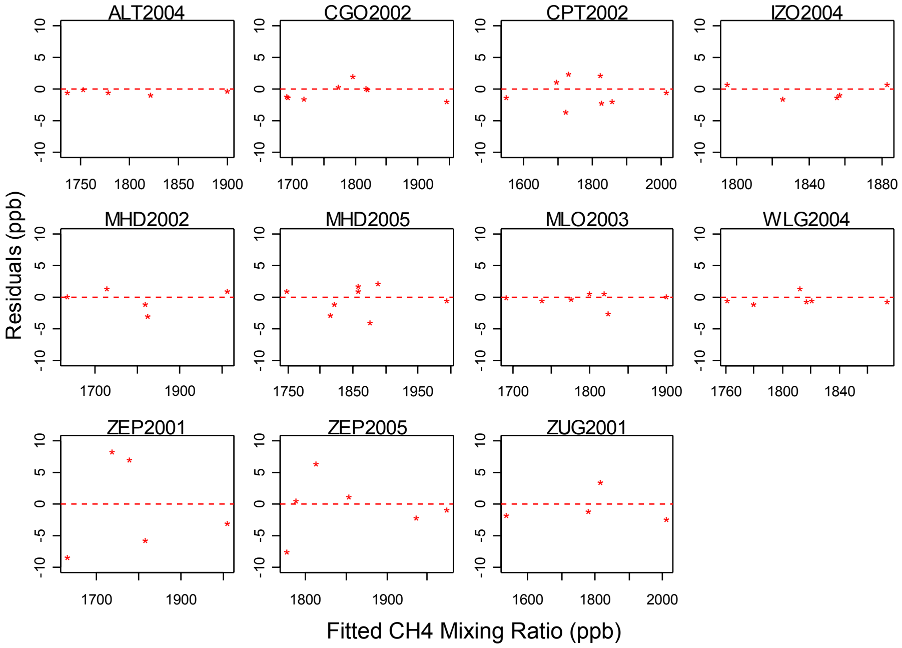

Figure 5: Tukey-Anscombe plots of regression residuals for CH4 inter-comparisons.

The result of calibration biases found during these audits is illustrated in Figure 6. Based on a target of a 0.5% maximum deviation between the station and WCC-Empa over the ambient concentration range at each individual site, the figure demonstrates compliance in all cases.

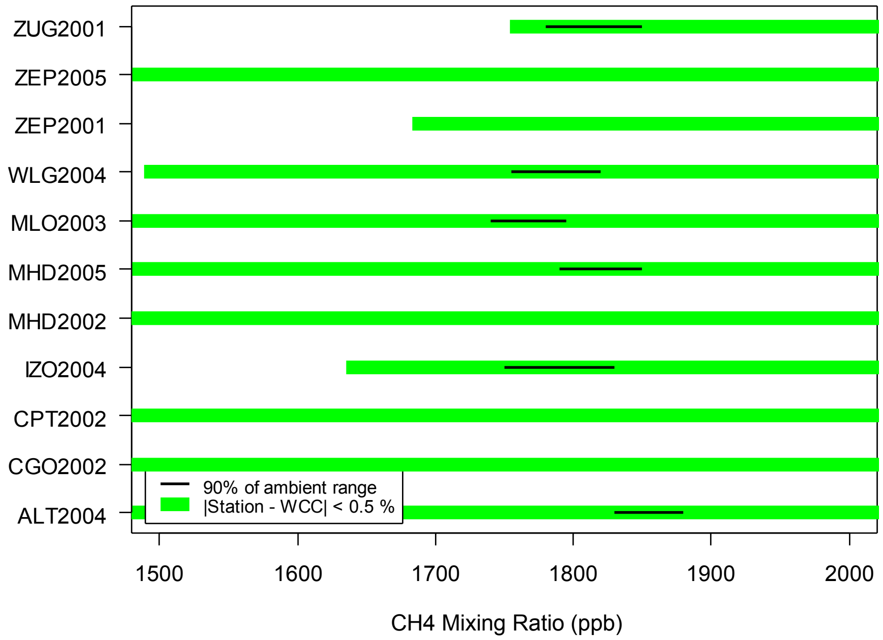

Figure 6: **Comparison of the ambient CH_4 concentration range (90% inter-percentile range) (black lines) with the range of calibration gases not exceeding a threshold absolute deviation of 1% between station and WCC-Empa, based on linear regression analyses (green bars).**

2.1.5 Conclusions and Recommendations

In general, it appears fair to say that the CH_4 network is currently in better control than the CO network. The observed slopes of the linear regression of station-assigned versus WCC-assigned mixing ratios range between 0.96 and 1.07 for CH_4, 0.84 and 1.31, for CO. However, it also fair to say that CO is a more difficult case because of scale issues and the possibility of non-linear response curves for the mercuric oxide reduction-type instruments. The scale issues mainly have to do with more severe drift of low concentration CO cylinders. The non-linear instrument response is sometimes an issue of non-awareness, but probably more often a simple cost issue, where sufficient resources are lacking to obtain a sufficient number of standards.

In our experience, audits and training raise awareness for QA/QC issues and help improve data quality. Regular inter-comparisons are considered necessary for adequate records and may support future data corrections.

CCL scale revisions need to be published officially, publicized better, and guidance given for data correction. Mechanisms to ensure traceability of stations to the CCL should be formalized and involve the yearly exchange of cylinders between CCL and WCC (RCC), as well as regular system and performance audits of stations by a WCC or RCC.

There is also a need to better integrate relevant regional and contributing stations in the GAW QA system, because the global base of observational data of known quality needs to be improved [Klausen, 2006]. It may be worthwhile to establish stronger links to national metrological institutes and to explore common interests. A first step towards including more stations in the GAW QA system should involve 'paper' audits of the system set-up and existing traceability chains of candidate stations. A major improvement of the GAW QA system for CO is expected from the SAG RG Guidance Document on CO. With regards to existing data at the World Data Centre for Greenhouse Gases, these should be better documented in terms of data versions, and for CO, a harmonized data set on a 'WMO-2006' scale should be an objective.

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2.2 Quality Assurance and Quality Control for N_2O

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2.2.1 Introduction

Contributions to global N_2O data originate from a number of different sources,: global and regional networks, individual GAW global and regional stations as well as other laboratories and sampling sites. Due to different calibration scales, the existing data cannot simply be merged. Coordinated Quality Assurance and Quality Control (QA/QC) are required when wanting to combine N_2O measurements from different sites and different monitoring programmes in order to increase the global data coverage. The ultimate goal is traceability to a single scale.

2.2.2 GAW Central Facilities and Elements of QA/QC

GAW facilities involved in QA/QC activities for N_2O comprise the Central Calibration Laboratory (CCL), Scientific Advisory Group for Greenhouse Gases (SAG GG), Quality Assurance/Science Activity Centre (QA/SAC Germany) and the World Calibration Centre for N_2O (WCC-N_2O). Details of concepts, tasks and responsibilities are described in WMO GAW Reports No. 142 and 156. Moreover, recent additional information is provided in Part II of the WMO GAW Report No. 165 (GAW 2005 Workshop).

The N_2O scale for GAW is maintained by the CCL (NOAA scale), to which the WCC-N_2O is linked. It is emphasized that the WCC-N_2O is not supposed to perform separate calibrations. The concept of traceability of calibrations is illustrated in Figure 1. The left part of the schematic shows the relationships in terms of institutions involved. The right part explains the hierarchy of standards. Standards on the tertiary level serve as laboratory standards for GAW laboratories and other participants and as travelling standards for round-robin experiments and audits.

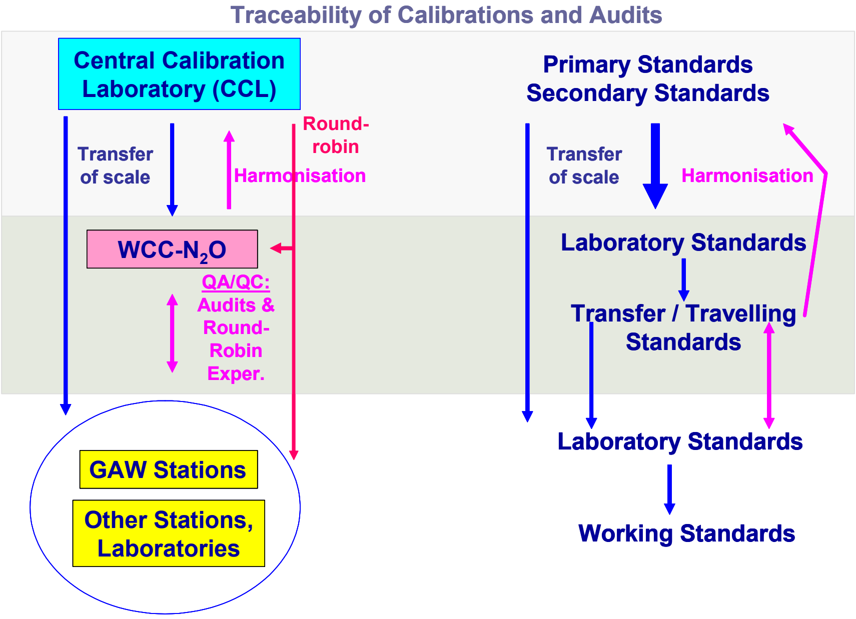

Figure 1: **Schematic of the traceability of calibrations, round-robin experiments and audits. The left part shows the relationships in terms of institutions involved, the right part explains the hierarchy of standards.**

Some details are noteworthy in order to illustrate both the long-term elements of QA/QC and recent activities. The CCL is responsible for the calibration of laboratory standards of participating laboratories for which these standards constitute the standards of the highest rank. In this sense, a recalibration of five standards and a first calibration of two additional standards of the

WCC-N_2O were performed in early 2005. In terms of round-robin experiments, IHALACE, the International HALocarbons in Air Comparison Experiment, also includes N_2O, and therefore the WCC-N_2O is among the participants of this round-robin. With respect to QA/QC for N_2O (as with other trace gases), a number of responsibilities are directly with the individual stations and laboratories. This includes the acquisition of an adequate number of calibration standards. Furthermore, internal quality control at a station by regular comparison of working standards with laboratory standards directly traceable to the standard scale, and ongoing intercomparisons of a station with another station or laboratory based on ambient air samples are required.

2.2.3 GAW Documents Related to QA/QC for N_2O

The preparation of Measurement Guidelines (MGs) has been an important part of the QA/QC work during recent years. The MGs for N_2O will form part of a future GAW Report containing guidelines for both CH_4 and N_2O, which could be patterned in a similar way. These "Guidelines for the Measurement and Quality Assurance of Methane and Nitrous Oxide" will also contain Data Quality Objectives (DQOs) for both species. In a separate chapter, representativeness criteria for trace gas measurements will be addressed. Another chapter on 'Practical Examples of Uncertainty Assessment' will contain a tutorial to familiarize the reader with this important topic. At present, the editing of some chapters of the MGs is still in progress. Future steps will include a careful review process of the draft, and finally approval by the SAG GG.

The measurement guidelines themselves provide information ranging from basic requirements for the set-up of N_2O measurements to data processing and submission to data centres. According to this general concept, the MGs are mainly intended for use at stations where measurements of N_2O have recently been added to the programme or will be in the future. Due to the complexity of high-quality N_2O measurements, no rigid Standard Operating Procedures (SOPs) can be compiled.

Terminology and definitions of terms are an important issue within GAW. Therefore a special chapter on these issues has been foreseen in the MGs. It is noted that the GAW Strategic Implementation Plan (GAW Report No. 142) recommends adoption and usage of internationally accepted methods and vocabulary to deal with measurement uncertainty as outlined in ISO publications. Currently, about 40 relevant terms are compiled in a glossary within the MGs. It deals partly with the ISO terminology, but also provides definitions of terms related more specifically to trace gas measurements. The main sources of information for the definitions were ISO publications. Some of the definitions in the glossary are directly adopted from the "International vocabulary of basic and general terms in metrology" (1993) and from the "Guide to the expression of uncertainty in measurement" (1995).

The terminology chapter of the MGs has been reviewed by two metrological scientists. The implementation of their comments and suggestions is still ongoing. The ultimate goal is to enlarge the existing draft by input from other GAW communities in order to step forward from an individual chapter of the CH_4/N_2O guidelines to a stand-alone GAW document with the envisaged title "A GAW Terminology and Definitions Standard for Measurement Guidelines".

2.2.4 Data Quality Objectives

DQOs for N_2O were defined by the SAG GG during its meeting in Toronto in September 2003. Based on discussions during the 13th Experts Meeting and the subsequent meeting of the SAG GG in September 2005, some modifications to the 2003 version of the DQOs were made. The main point emerging from the discussions was that the defined targets were considered too generous. Here an updated version of the DQOs is briefly summarized as follows:

Instrumental precision: The repeatability (1 standard deviation) should be better than ± 0.2 ppb, and reproducibility better than ± 0.3 ppb at ambient levels of N_2O. The target value, as driven by scientific requirements, is 0.1 ppb.

Relevant range of N_2O mole fractions: To determine the response function of an analytical system, six (minimum five) different N_2O standards with mole fractions between 290 and 350 ppb are requested. For ambient measurements, the most important range is between 310 and 330 ppb, for which more stringent objectives are set out than for the upper and lower wings (see below).

Uncertainty of ambient N_2O measurements: The uncertainty associated with ambient N_2O measurements can be separated into contributions related to instrumental precision, uncertainty associated with the standard scale as well as accuracy of the working standards employed at a specific site. Uncertainty will be estimated by intercomparisons with standards within a round-robin experiment or intercomparisons as part of an audit. Such exercises will determine if measurements at different sites and from different institutions are on the GAW N_2O standard scale.

With respect to intercomparison objectives, the following goals have been defined. These will determine the network or interlaboratory comparability of N_2O measurements.
(i) The recommended comparability is ± 0.2 ppb. Maximum acceptable deviations from assigned values are 0.5 ppb for the range 310 - 330 ppb, and 0.8 ppb for the upper and lower wings. Uncertainties larger than 0.5 ppb in the range 310 - 330 ppb, and 0.8 ppb for the upper and lower wings can be included in the database, but should be flagged.
(ii) Target Data Quality Objectives for the future will request a maximum uncertainty of 0.1 ppb for the entire range of 290 to 350 ppb.

2.2.5 Status with Respect to QA Tasks of the Strategic Plan

The Addendum to the GAW Strategic Plan (WMO GAW Report No. 156) has set out a number of tasks of which some also pertain to N_2O. The status of N_2O-related work as of September 2005 is briefly summarized as follows: Task 1: The draft of the requested technical document for international terminology is nearly ready for the purposes of CH_4/N_2O, which means it should be suitable for most greenhouse gases. Some more edits will be necessary before it is ready for use by all GAW communities, which in turn might then make additions according to their specific needs. Task 2: Data Quality Objectives have been approved by the SAG GG. However, some further discussions will still be necessary. Task 3: The CCL and WCC-N_2O have been established and are operational. Task 4: Measurement Guidelines for N_2O are at an advanced stage, but not yet officially approved. Task 5: Separate Guidelines for audits are currently under discussion, involving mainly WCC-EMPA and WCC-N_2O. Finally, the task "Training, etc" listed in Report No. 156 has been fulfilled by contributions to GAWTEC, which will also continue in the future.

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2.3 Current Status and Advances of WDCGG Operation of the World Data Centre for Greenhouse Gases

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Japan Meteorological Agency

2.3.1 Introduction

The World Data Centre for Greenhouse Gases (WDCGG), first established in 1990, has now been operating for more than 15 years. The amount of observational data submitted to and subsequently released by the WDCGG have increased markedly with recent developments in data processing technology and telecommunications network infrastructure, such as the internet. Furthermore, the data management of the WDCGG and information demands on the WDCGG have changed. Therefore, the "Data Reporting Manual of the WMO World Data Centre for Greenhouse Gases" (WDCGG No.1) published in 1991, which describes the operation of the WDCGG and data submission formats, has become unsuitable for the current operations of the Centre.

Since the United Nations Framework Convention on Climate Change (UNFCCC) came into force in 1994, which has systematized the observation of greenhouse gases, concern regarding climate change issues has increased among not only scientists but also the general public. Furthermore, concerns regarding greenhouse and related gases have increased since the Kyoto Protocol came into force in 2005.

Under the circumstances mentioned above, the WDCGG plans to newly publish the WDCGG data submission and dissemination guide for the following purposes:

- To introduce the overall activities of the WDCGG to respond to the social concerns of not only observers and the scientific community but also the public.
- To clarify the purposes, function, and operational courses of the WDCGG to make better use of archive data.

2.3.2 Current Status of WDCGG Operation

2.3.2.1 Operations of the WDCGG

The current operations of the WDCGG are composed of the following four functions:

- To collect reliable measurement data and associated metadata from the GAW observation network and relevant international research programmes,
- To archive these data continuously for long-term use,
- To produce WDCGG diagnostic products in which the latest trends in greenhouse gas concentrations and the situations of observation sites are summarized,
- To provide archive data and various other diagnostic products to allow users easy access, such as the Internet or periodical publications.

So far, 312 sites in 66 countries submit data (Figure 1). Data submitting sites and the total amount of data have been increasing. Particularly, submissions of other greenhouse gases and related gases have significantly increased in a few years (Figure 2).

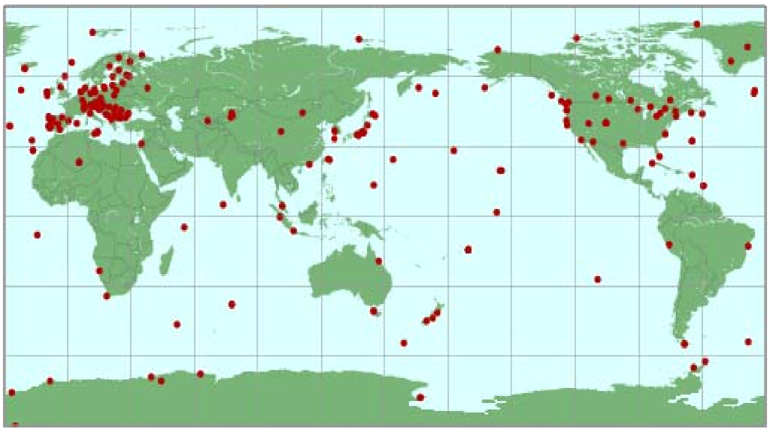

Figure 1: **Location map of data submitting sites (except mobile sites).**

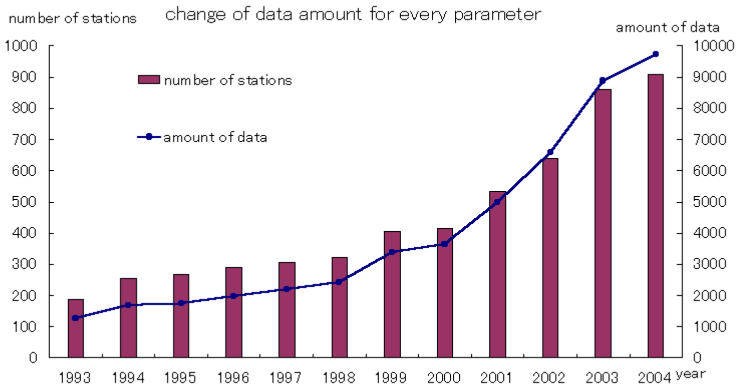

Figure 2: **Annual variation of submitted data.**

2.3.2.2 Contents of the WDCGG Data Summary

The WDCGG Data Summary, which summarizes the current situations of greenhouse gases, is published every year. Analyses including the global mean mixing ratios and growth rates of greenhouse gases (CO_2, CH_4, N_2O, etc.), the three dimensional representations of latitudinal distributions (carpet) of CO_2, CH_4, CO, and etc. are presented in this summary. The WDCGG Data Summary and other publications can be downloaded from the "Publication" page on the WDCGG website (http://gaw.kishou.go.jp/wdcgg.html).

2.3.3 Current Issues for WDCGG

- Rapid increases of data amount and kinds of species.
- Quality of archive data is not homogeneous.
- Collection of data is insufficient, particularly for ocean data.
- Complicated procedures for access to archived data and other content on the WDCGG website.

The WDCGG needs clear operational concepts, definite data formats, and arrangement of content distributed to promote data submission and data utilization. The WDCGG plans to publish a new WDCGG data submission and dissemination guide.

2.3.4 Main Points to the New Guide

2.3.4.1 Definition

Fundamental concepts and terms used in this guide (*e.g.* WDCGG ID, Observation data, Quality flag, and Archive data) are defined.

2.3.4.2 Definite data formats for submission data

The data formats for submission data are newly defined. However, submitting data with the current data submission formant is accepted for current data submission sites.

2.3.4.2.1 Structure of data format

The data formats for submission data commonly consist of “file name”, “header”, and “data”.

2.3.4.2.2 Categories of data format

The WDCGG has adopted the following five format categories:

1. Air sampling observations at fixed site (hourly mean, monthly mean, yearly mean, instantaneous, accumulated).
2. Air sampling at mobile platforms (*e.g.* aircraft, ships).
3. Sampling of surface seawater and the overlying atmosphere (new format based on IOC/IOCCP recommendation).
4. Sampling of gases trapped in ice cores (improved format).
5. Hydrographic sampling (new format based on WOCE format).

2.3.4.2.3 New data classification for mobile platforms

The WDCGG adopts following three classification of data format for mobile platforms:

1. Atmospheric data.
2. Surface seawater data.
3. Hydrographic data.

2.3.4.3 Improvement of metadata archive

The WDCGG has made improvements in the archival of metadata. The contents of metadata are classified as follows:

1. Information on submitter.
2. Information on site – (a) location, (b) geography, (c) surroundings (including potential sources and sinks).
3. Information on parameters (a) measurement (including system and operation), (b) calibration (including using scale, maintenance, and frequency), (c) data and data processing (including methods and quality flag).

2.3.4.4 Harmonization of WDCGG archive data

The harmonization of data quality is a serious matter for data users. The WDCGG plans to perform minimum checks on submitted data and provide feedback to the sites before data acceptance, when necessary, in collaboration with the Science Advisory Group for Greenhouse Gases (SAG GG). Furthermore, a reliable dataset for the global analyses of greenhouse gases is required for the WDCGG. The WDCGG plans to create a dataset of background sites with traceability and the screening methods authorized by the SAG GG.

2.3.5 Improvement of the WDCGG website

The WDCGG website will be arranged for easy access by users.

2.3.6 Release Schedule of the WDCGG Data Submission and Dissemination Guide

Using the new formants for submitting and providing data will start six months after the publication of the new guide. Submitting data with the current data submission formant is accepted for current data submission sites. The new formants will be applied to submissions from new sites and submissions of new parameters.

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2.4 Flask Air Sampling Programmes at the Alert GHG Comparison Site

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Environment Canada

2.4.1 Abstract

Scientists present at the 13th WMO/IAEA Meeting of Experts on Carbon Dioxide Concentration and Related Tracers Measurement Techniques, September 19-22, 2005 in Boulder, CO, U.S.A., recommended the WMO/GAW sites at Alert, Mauna Loa and Cape Grim serve as Greenhouse Gas (GHG) Comparison Stations. Various comparison programmes are currently conducted at Alert, including direct, indirect and flask – *in situ* comparisons. These comparison exercises will provide a mechanism to link many individual networks and improve global atmospheric carbon estimates. This report provides an update on the GHG flask air sampling programmes and inter-comparison activities conducted at Alert.

2.4.2 Introduction

High precision atmospheric measurements in greenhouse gas (GHG) concentrations and CO_2 isotopes ($\delta^{13}C$ and $\delta^{18}O$) provide valuable information in determining the magnitude and distribution of carbon sources and sinks and in improving our understanding on various controlling processes on regional and global scales. Systematic biases amongst various data sets (obtained from different laboratories) may lead to improper carbon budget estimates. The assessment of a global network comparability level (see Recommendations section) is an important but challenging exercise to the atmospheric GHG measurement community. In the past, network comparability has typically been evaluated by circulation and analysis of high pressure cylinders amongst participating laboratories (i.e. WMO Round Robin). Although a very useful exercise, results obtained during these experiments did not necessarily translate to similar results on flask measurements [*Masarie et al*., 2001]. To improve the network comparability levels, flask air inter-comparison experiments had been strongly encouraged by the participants in the 12th WMO/IAEA Expert Meeting's recommendation, including programmes such as the TACOS Sausage flask comparison and flask air comparisons at selected "Super Sites".

The establishment of three international GHG comparison sites provides a unique opportunity for the GHG measurement community to link global measurement programmes and provide an opportunity for individual participating laboratories to assess their measurement and data quality. These inter-comparison programmes are intended to run long-term and thus provide a regular ongoing check. Examples of Inter-Comparison Project (ICP) exercises include:

1. <u>Direct flask-ICP:</u> Analysis of air in the same flask by two different laboratories. Information from these exercises can uniquely identify problems associated with analytical procedures, and standard traceability. It does not assess sample integrity (i.e. whether the flask air sample is contaminated or fractionated).
2. <u>Flask – *in situ* measurements ICP:</u> Comparison of hourly averaged *in situ* measurements with flask measurements. Can identify problems with the *in situ* measurement system, including standard scale propagation errors. This is particularly true if more than one flask programme is available to compare the *in situ* data with. It can also provide information pertaining to problems associated with flask sampling procedures, e.g. fractionation, contamination or shipping.
3. <u>Indirect flask ICP:</u> Comparison of two individual sets of flasks sampled at the same location and as close to each other in time as possible and measured by the two participating laboratories. This comparison provides information more closely tied to the "real" network.

The combination of indirect and direct flask ICPs as well as flask- *in situ* measurement ICP should provide sufficient data to identify and addressed associated sampling and analysis errors.

2.4.3 *Site Description*

As part of a global network under the auspices of the World Meteorological Organization's (WMO) Global Atmosphere Watch (GAW) Programme, Environment Canada (EC) established a baseline air chemistry observatory in 1986 at Alert, Nunavut (82°28'N, 62°30'W) located on the northern tip of Ellesmere Island in the Canadian Arctic (Figure 1). The primary function is to monitor the mixing ratios of trace atmospheric constituents thought to have an impact on climate. It is the most northerly observing station in the GAW network, and, as such, it is far removed from the major industrial regions of the northern hemisphere. The Observatory is situated ~ 6 km south of the main Alert camp on a plateau 210 m above sea level. The degree of contamination from the local environment is minimal with less than 4% of the winds originating from within ENE camp sector [Worthy et al, 1994]. A few kilometers to the south-east are hills 800 m high, and further to the west are mountains rising to an altitude of 1500 m. The land around Alert is covered with snow for almost ten months of the year and has a sparse covering of polar desert vegetation in the summer. Alert's isolated location is ideally situated for the monitoring of global atmospheric pollutants. If pollutants are present in the atmosphere at Alert, then they represent a contribution to the background pollution of the Northern Hemisphere as a whole. In addition to GHG measurements, many other atmospheric observations are carried out at Alert by EC and other international organizations, including aerosol chemistry, O_3, volatile organic compounds (VOCs) and peroxyacetylnitrate (PAN). (Worthy et al, 2003).

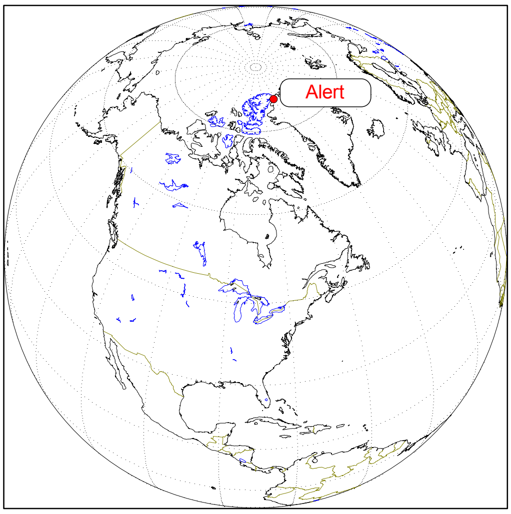

Figure 1: **Location of the Alert baseline measurement site.**

2.4.4 *Flask Sampling Programmes at Alert*

EC in collaboration with the Institute of Ocean Sciences (IOS), Canada, implemented weekly flask sampling for carbon dioxide (CO_2) in 1975 at the Alert Weather Station. Over time, other programmes were established at Alert, including flask sampling for CO_2 (and other gases and isotopes) by the Scripps Institution of Oceanography (SIO) in 1984, NOAA/ CMDL in 1985 and CSIRO in 1988. In August, 1986, EC established the Alert Global Atmosphere Watch (GAW) Observatory, Canada's first research station for the continuous monitoring of atmospheric trace gases and aerosols. In 1988, EC assumed responsibility from IOS for the flask sampling network at Alert as well as from other sites in Canada.

Currently, seven individual flask sampling programmes for GHGs measurements are conducted at Alert by both EC and International partners (Table 1), and an additional flask programme is being planned in 2006. All programmes are conducted via different sampling systems and protocols (see Table 2 and Figures 2-6), implemented by each respective network. Four agencies, as indicated in the last column of Table 1, currently participate in direct flask ICPs with EC. The first ICP was implemented at Alert in 1997 between CSIRO Marine and Atmospheric Research (CMAR) and EC for CO_2 isotopes ($\delta^{13}C$ and $\delta^{18}O$). Details and results on this programme can be found in *Huang et al.,* [2002] and *Langenfeld et al.,* [2003]. This programme initially entailed additional EC owned flasks being sampled at Alert and first sent to CMAR for gas concentrations (i.e. CO_2, CH_4, CO, H_2, N_2O) and CO_2 isotopes ($\delta^{13}C$ and $\delta^{18}O$) analysis. The flasks were returned to EC for CO_2 isotope analysis only. In 2002, the CMAR/EC ICP programme was expanded to include the analysis of CO_2, CH_4, CO, H_2 and N_2O at EC as well. The second direct ICP was implemented at Alert in 1998 between NOAA and EC. This included an additional pair of NOAA owned 2.5 L flasks being sampled each week (for a total of 4 flasks each week). Two of the flasks are analyzed at EC for CO_2, CH_4, CO, H_2, N_2O and SF_6 before being sent to NOAA for CO_2, SF_6, CH_4, CO, H_2, N_2O and $\delta^{13}C$ and $\delta^{18}O$ in CO_2. An automated extraction line is currently being developed at EC. This will reduce the volume of sample air required for CO_2 isotope analysis on the NOAA owned flasks, then, an ICP with NOAA/INSTAAR can be implemented. Presently, EC can only participate in the ICP activities for CO_2 isotopes when the sample analysis terminates at EC because all the remaining air in the flask is required for sample preparation.

Table 1: **Flask air sampling programmes for GHGs carried out at the Alert Observatory.**

Measurement Suite	Sampling Record	Agency	Direct ICP with EC
CO_2	1975 -	Environment Canada	n/a
CO_2, CH_4, CO, N_2O, SF_6, H_2	2000 -	Environment Canada	n/a
$\delta^{13}C$ and $\delta^{18}O$ in CO_2	1997 -	Environment Canada	n/a
CO_2, CH_4, CO, N_2O, SF_6, H_2	1988, 1991 & 1992 -	CSIRO, Australia	Yes (since 2002)
$\delta^{13}C$ and $\delta^{18}O$ in CO_2	1988 -	CSIRO, Australia	Yes (since 1997)
CO_2, CH_4, CO, N_2O, SF_6, H_2	1985, 92 & 97-	NOAA, USA	Yes (since 2001)
$\delta^{13}C$ and $\delta^{18}O$ in CO_2	1992 -	NOAA, USA	Planned in 2007
CO_2	1984 -	SIO, USA	No
$\delta^{13}C$ and $\delta^{18}O$ in CO_2	1984 -	SIO, USA	No
O_2/N_2	1989 -	SIO, USA	No
CO_2	1995 -	IOS, Canada	No
$\delta^{13}C$ and $\delta^{18}O$ in CO_2	1995 -	IOS, Canada	No
CO_2, CH_4, CO, N_2O, SF_6, H_2	2004 -	MPI, Gernmany	Yes (since 2004)
$\delta^{13}C$ and $\delta^{18}O$ in CO_2	2004 -	MPI, Gernmany	Yes (since 2004)
CO_2, CH_4, CO, N_2O, SF_6, H_2	2004 -	U. of Heidelberg, Gernmany	Yes (since 2004)
$\delta^{13}C$ and $\delta^{18}O$ in CO_2	2004 -	U. of Heidelberg, Gernmany	No
CO_2, CH_4, CO, N_2O, SF_6, H_2	Planned in 2006	LCSE, France	Yes (planned in 2006)
$\delta^{13}C$ and $\delta^{18}O$ in CO_2	Planned in 2006	LCSE, France	No

In October 2004, a third flask ICP programme was initiated at Alert between EC and the Max Planck Institute (MPI) in Jena, Germany. This programme entails 3 MPI owned 0.5 L glass flasks being sampled every other week. One flask (from the trio) is first analyzed at EC for CO_2, CH_4, CO, H_2, N_2O, and SF_6. All 3 flasks are analyzed at MPI for the same suite of gases as well as O_2/N_2, Ar/N_2 and for CO_2 isotopes ($\delta^{13}C$ and $\delta^{18}O$). One of the trio flasks are returned back to EC for CO_2 isotopes ($\delta^{13}C$ and $\delta^{18}O$) analysis. In October 2004, as well, the fourth flask ICP programme was implemented at Alert between EC and the University of Heidelberg (UofH), Germany. This programme entails two UofH owned 0.5 L glass flasks being sampled every week using the EC sampling system. One flask of the pair is analyzed at EC for CO_2, CH_4, CO, H_2, N_2O, and SF_6. Both flasks are then shipped to UofH and analyzed for CO_2, CH_4, CO, H_2, N_2O, and SF_6 and CO_2 isotopes ($\delta^{13}C$ and $\delta^{18}O$). In October 2006, the fifth flask ICP programme at Alert is being planned between EC and the Laboratoire des Sciences du Climat et de l'Environnement (LSCE), Gif-sur-Yvette, France. A sampling, flask type and analysis arrangement similar to the EC/UofH ICP programme is being envisioned.

At Alert, all flasks are sampled on the same day and as close to each other in time as possible. Complete sampling is typically completed within a 2-3 hour window. The coordinated sampling schedule is listed in Table 2. It should be noted that sampling collection only occurs when winds originate from the prevailing SW wind sector and with wind speeds greater than 1.5 m/s. Photos of the various sampling systems for SIO, NOAA, EC and MPI are shown in Figures 2 to 6 (taken in 2004). The UofH is sharing the EC sampling system. LSCE will install their own dedicated sampling system and share the same cryogenic cooling system used by SIO and EC.

Table 2: Current flask air sampling protocol and schedule at Alert.

Week#	Sampling order# & duration (min)	Sampling Inside of the lab		Sampling Outside of the lab
		via the Original SIO Inlet	via the Aspirator Inlet	
[1]	**1.** (75 mins for SIO & 45 mins for MPI)	SIO (3×5L, biweekly)	MPI (3×1L, bi-weekly)	
	2. (50 mins)	EC (2×2L, weekly)		NOAA suitcase (2×2.5L, weekly)
	3. (50 mins)	EC/CSIRO-ICP (2×2L, weekly May-Oct. biweekly rest of year)		SIO (2×5L, pair, weekly)
	4. (30 mins)	Universtiy of Heidelburg (2×1L, weekly)		IOS, Victoria, BC (2×5L, biweekly)
[2]	**1.** (50 mins)	EC (2×2L, weekly)		NOAA suitcase (2×2.5L, weekly)
	2. (50 mins)	EC/CSIRO-ICP (2×2L, weekly May-Oct. biweekly rest of year)		SIO (2×5L, pair, weekly)
	3. (30 mins)	Universtiy of Heidelburg (2×1L, weekly)		
[3]	**1.** (45 mins for MPI & 75 mins for SIO)	MPI (3×1L, bi-weekly)	SIO (3×5L, biweekly)	
	2. (50 mins)	EC (2×2L, weekly)		NOAA suitcase (2×2.5L, weekly)
	3. (50 mins)	EC/CSIRO-ICP (2×2L, weekly May-Oct. biweekly rest of year)		SIO (2×5L, pair, weekly)
	4. (30 mins)	Universtiy of Heidelburg (2×1L, weekly)		IOS, Victoria, BC (2×5L, biweekly)
[4]	**1.** (50 mins)	EC (2×2L, weekly)		NOAA suitcase (2×2.5L, weekly)
	2. (50 mins)	EC/CSIRO-ICP (2×2L, weekly May-Oct. biweekly rest of year)		SIO (2×5L, pair, weekly)
	3. (30 mins)	Universtiy of Heidelburg (2×1L, weekly)		

2.4.5 Summary

In order to improve our understanding in carbon cycling via atmospheric measurements of CO_2 and inversion modelling, it has been recognized that a Northern Hemisphere network comparability level of 0.1 ppm for CO_2 is desired. WMO recommended network precision requirements have also been assigned for CH_4, CO, N_2O, $\delta^{13}C$-CO_2 and $\delta^{18}O$-CO_2 (see recommendations section in this issue). The recommendation of establishing three GHG comparison site provides an opportunity to assess network comparability. Eight flask sampling programmes are currently being conducted at Alert, including direct, indirect and flask – *in situ* comparisons. The results from these ICP programmes may provide a level of confidence in the accuracy of these atmospheric measurements and reveal participating laboratories that require attention in order to meet WMO measurement target objectives. Results of all comparison activities at Alert will be summarized in the meeting report from the 14th WMO/IAEA Meeting of Experts on Carbon Dioxide Concentration and Related Tracers Measurement Techniques in 2007 in Helsinki, Finland. Results of intercomparison activities with NOAA/EC and CSIRO/EC at Alert have been previously reported in *Worthy et al [*2005], *Huang et al.,* [2002] and *Langenfeld et al.,* [2003].

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Worthy, D E. J. The Canadian Baseline Programme. In: Canadian Baseline Programme; Summary of progress to 2002, Meteorological Service of Canada, Chapter 1, pages 1-7, 2003.

Figure 2: **Photo of NOAA's Flask sampling suitcase. Sampling is conducted two hundred meters upwind of the laboratory.**

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Figure 3: **Photo showing the air sampling of a flask from the Scripps Institute of Oceanography. Sampling is conducted two hundred meters upwind of the laboratory.**

Figure 4: **Photo showing the flask sampling apparatus from the Scripps Institute of Oceanography for O_2/N_2 measurements. Sample air is drawn inside (from the top of a 10m tower) the laboratory using 3/8" Dekaron tubing.**

Figure 5: **Photo showing the flask sampling apparatus from Environment Canada. Sample air is drawn inside (from the top of a 10m tower) the laboratory using 3/8” Dekaron tubing.**

Figure 6: **Photo showing the flask sampling apparatus from the Max-Planck Institute, Jena Germany. Sample air is drawn inside (from the top of a 10m tower) the laboratory using 3/8” Dekaron tubing.**

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3. INSTRUMENTATION

3.1 CARIBOU: New Instruments For Continuous CO_2 Measurements and On-Line Data Transmission

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[3]Indian Institute of Astrophysics

3.1.1 Introduction

LSCE has started the implementation of a new network of continuous CO_2 monitoring stations, named CARIBOU. These instruments will upgrade and extend the existing RAMCES French network for atmospheric greenhouse gas monitoring (*Schmidt et al, these proceedings*). The new Caribou stations are designed to feature high precision measurements (reproducibility of the order of 0.01 ppm), high hardware reliability, and to require low maintenance. The design also allows the full remote control of the instrument, as well as automated data retrieval and on-line display capability.

Two such stations are already operational. The first one is located at Biscarrosse, France (44°22 40,6 N,1°13 52,5 W , inlet 116 m above sea level) The second one is located at Hanle, India (32°46 N, 78°57 E, 4517 m asl). The third one will be installed in the beginning of 2006 near Orleans, France. The current LSCE plans imply the manufacturing and the installation of more such instruments in the coming years.

3.1.2 CARIBOU Instruments Description

Each CARIBOU system consists of two main subsystems: a) An analysis compartment (shown in Figure 1), which includes a commercial LICOR analyser, pressure, flow and temperature regulators controlled by a Programmable Logic Controller (PLC), and an industrial PC used to configure and control the experiment; b) A pumping unit, which includes the pumps for up to three air inlets, and a refrigerator for preliminary drying of the air to be analysed.

Figure 1: View of the analysis compartment. Industrial standards have been chosen for high robustness, and easy maintainability.

The Caribou principles were inspired from the CSIRO Loflo analyser *(DA COSTA et al. 1997).* A schematic view of the system is shown in Figure 2. The LICOR-6252 was a commercially available dual-cell NDIR analyser. It has been chosen for the first three CARIBOU systems, but as the manufacturer is not selling it anymore, it will be replaced by a LICOR-7000 for the next stations.

The CARIBOU regulates the flow in the sample and reference cells (20 ml/min) and the pressure inside the cells (1080 mbar near sea level, 660 mbar at Hanle) with fuzzy logic algorithms. The box containing the LICOR analyser and the hardware necessary to regulate the gas flow and pressure is thermally regulated, and there is an additional temperature control of the LICOR cells themselves. The thermal and pressure control of the instrument minimizes the drift of the instrument, allowing calibrations to occur between once per week and once per month. The low flow of 20 ml/min allows the reference gas tank to last 5-6 months.

Three such systems have already been built. The first one was installed in May, 2005 at Biscarrosse, France, in a tower of the CELM (Centre d'Essai de Lancement de Missiles) military centre, and has been used for a Carboeurope regional intensive experiment in May-June 2005. The second one has been installed at the Indian Astronomical Observatory in Hanle in August 2005. The last one is still undergoing testing at LSCE, and it should soon equip a 200 m tower near Orleans, France, in the framework of the Chiotto project.

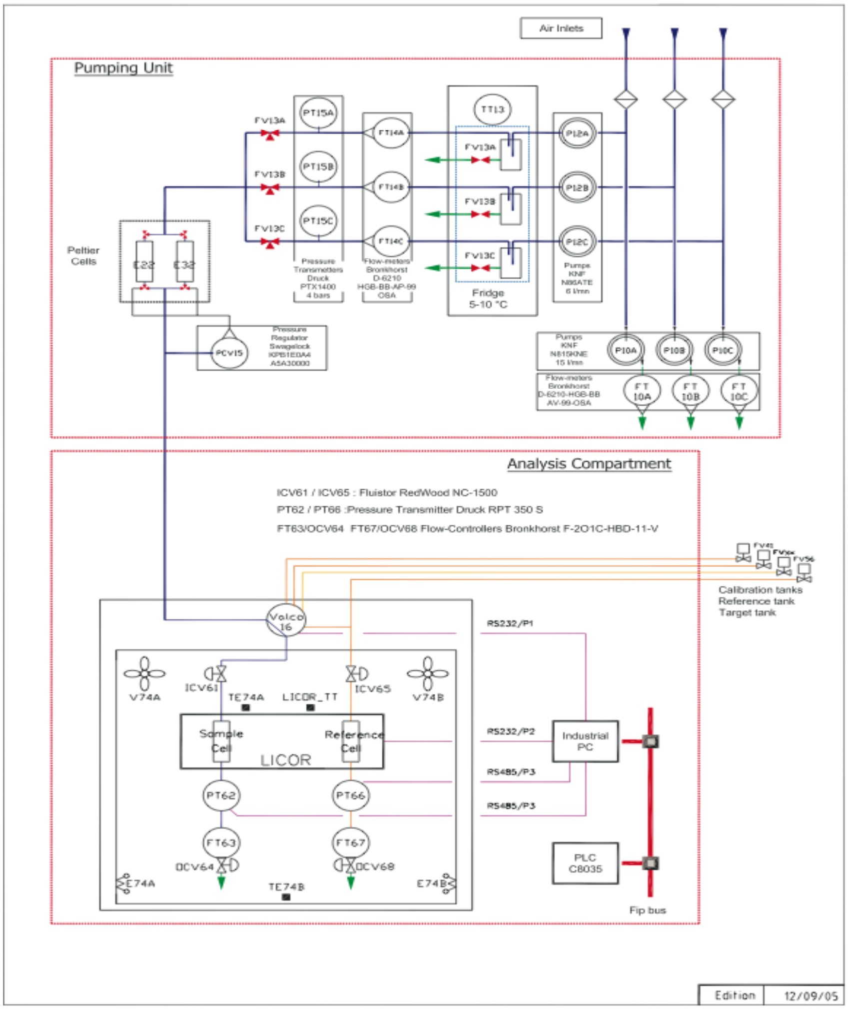

Figure 2: **CARIBOU Schematics (3 air levels version).**

3.1.3 ON-LINE DATA Transmission and Remote Control

For now, the CO_2 station network consists of 3 targets: Biscarrosse, Hanle and Orleans in April 2006 (see Figure 4). The architecture is shown on Figure 3. Each Caribou station has its own control system. A network link to the Saclay CEA centre allows remote supervision, configuration and maintenance. In case Internet is not available, a modem over a telephone line can be used instead.

The raw data are downloaded automatically every day or more frequently if needed by a central computer located at LSCE, which also allows for database operations. This computer is also in charge of daily tasks such as making connections or checking station health, and it will trigger alarms or warnings in case any abnormal condition is detected (for example, in case of bad pressure or temperature regulation, or low pressure in any standard gas cylinder).

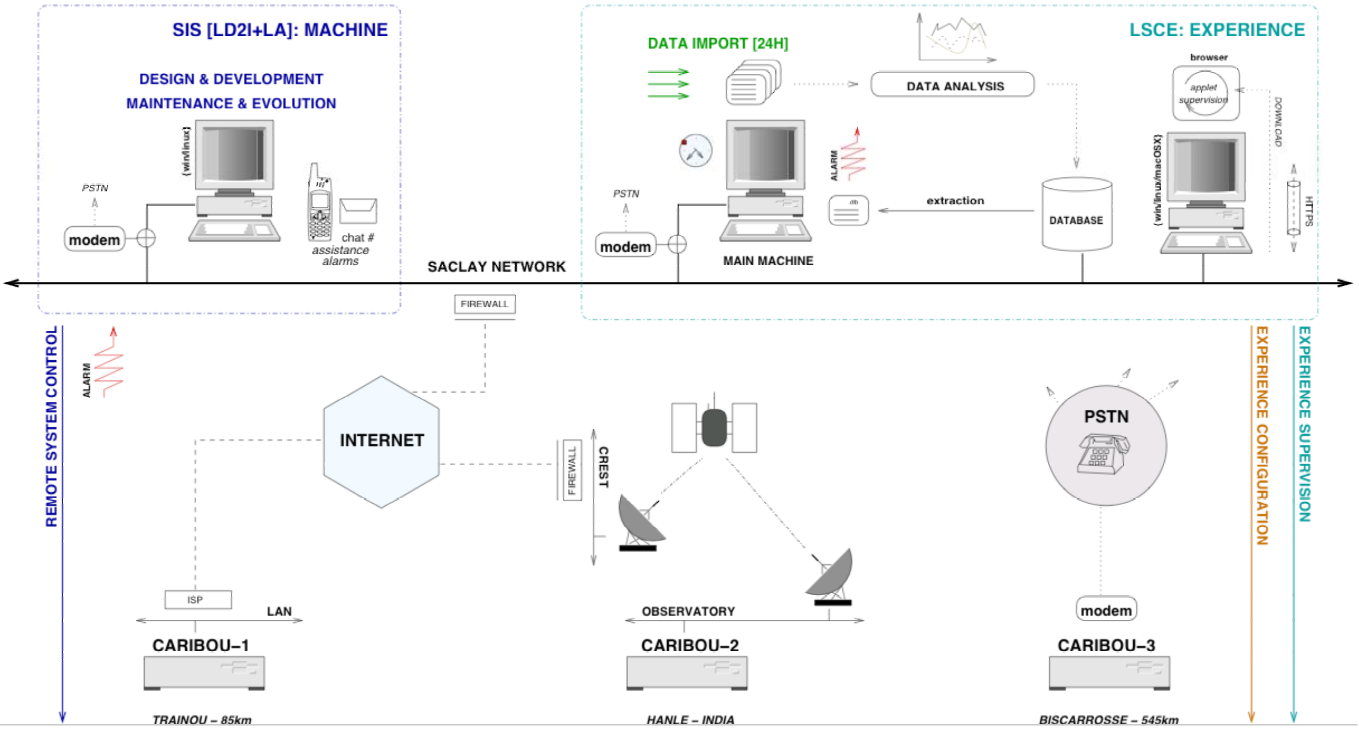

Figure 3: **Caribou network architecture: a distributed system controlled from Saclay.**

The Caribou software system is based on an industrial PC running Windows XP embedded on a flash disk. The core system is the control-command ANIBUS-FBI framework. This is a CEA-DAPNIA software that has been deployed for 15 years in more than 30 physics experiments. More than 500 variables are defined to handle and monitor the system such as cylinder pressures, Licor internal temperature or scheduler state. Among them, there is an on-line quick look CO_2 value with a +/-0.5 ppm precision (0.17 ppm rms). Email or phone alarms may be triggered on the most sensitive variables to notify remote operators that something is wrong. A history feature permits users to inspect all installation parameters during the last twelve months, with a default 10s temporal resolution, to make *a posteriori* analysis.

As far as slow processes are concerned, serial device management, scheduler and acquisition codes are implemented as Java services. For the experienced user, a tool allows one to define, tune or check all parameters of the CO_2 configuration: for example, standard tank connections, pattern definition, and experience scheduling. The application is available locally or remotely thanks to the applet mechanism without any special installation. Some additional utilities (remote desktop, file transfer, text and voice chat, web cam, etc.) may also make local/remote maintenance easier. A removable disk is used for the continuous storage of the scientific data, and of all the variables of the slow control .In case of a crash, automated production and installation of a versioned release will contribute to maximize machine availability as well as to simplify new future deployments.

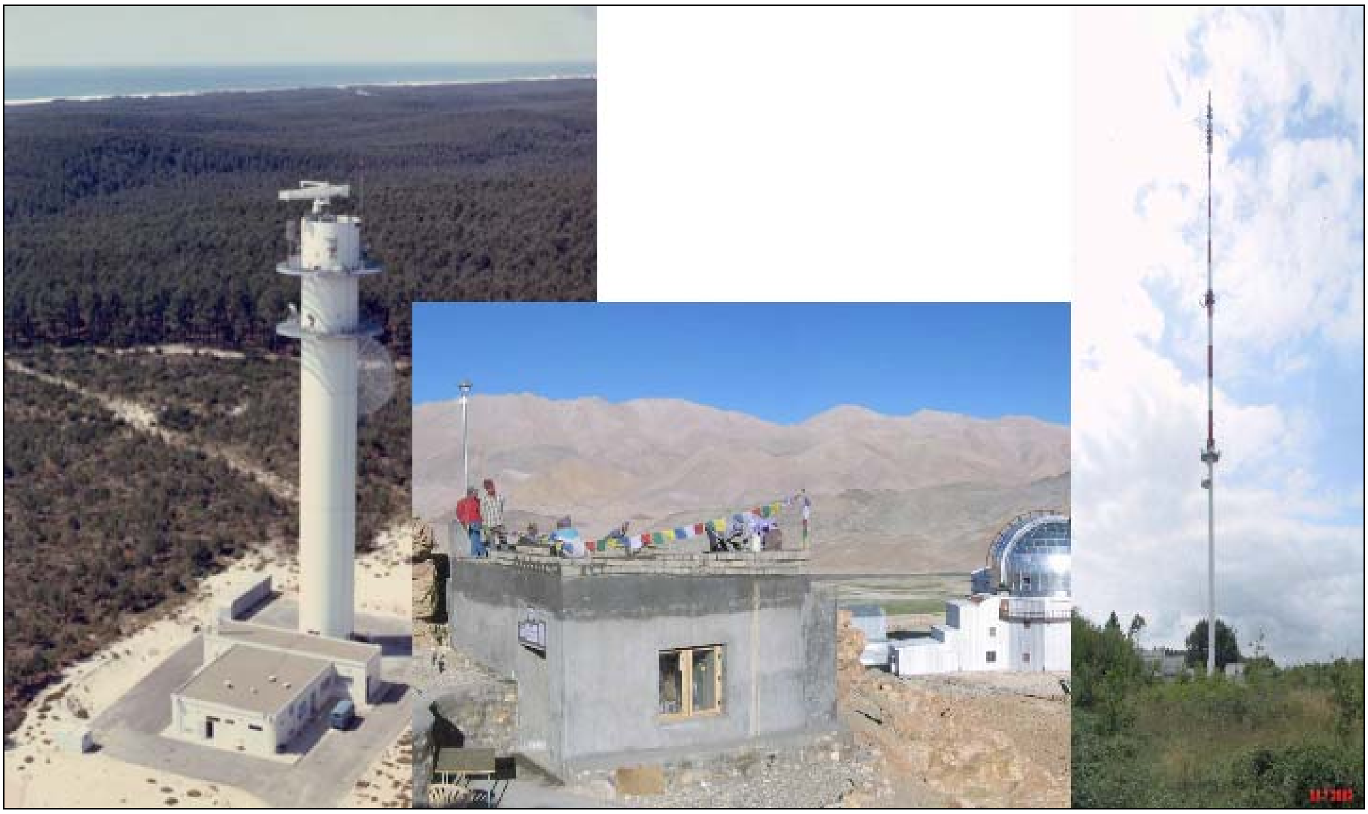

Figure 4: **View of the CARIBOU stations sites. From left to right: Biscarrosse, (France), Hanle (India), Le Trainou (France).**

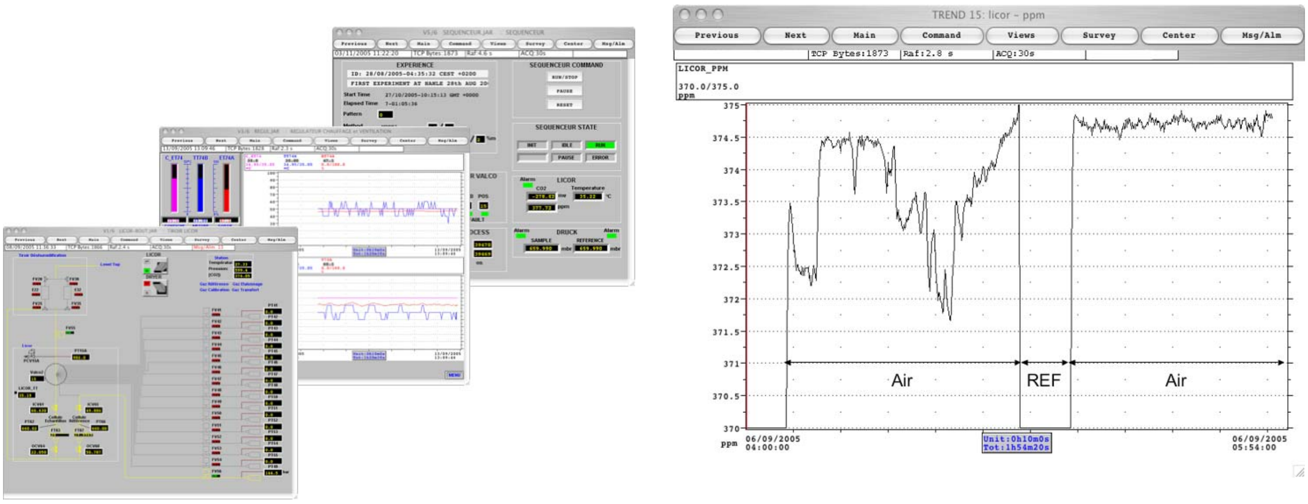

Figure 5: **Examples of on-line displays: left, a subset of control windows is shown; right, the on-line CO_2 curve is displayed.**

3.1.4 *Instrument Operation - Preliminary Performance*

Figure 6 gives an example of “characterization” measurements made at the LSCE laboratory: In this experiment, 3 standard tanks, and the reference tank, were measured sequentially over two weeks. The instrument calibration curve was determined one time and was fixed for this experiment. The instrument drift was taken as the signal measured on the reference tank, and was subtracted from the other tanks measurements. Except for tank #W413, which had a tiny leak at its regulator, the reproducibility of the measurements is of the order of 0.02 ppm (rms).

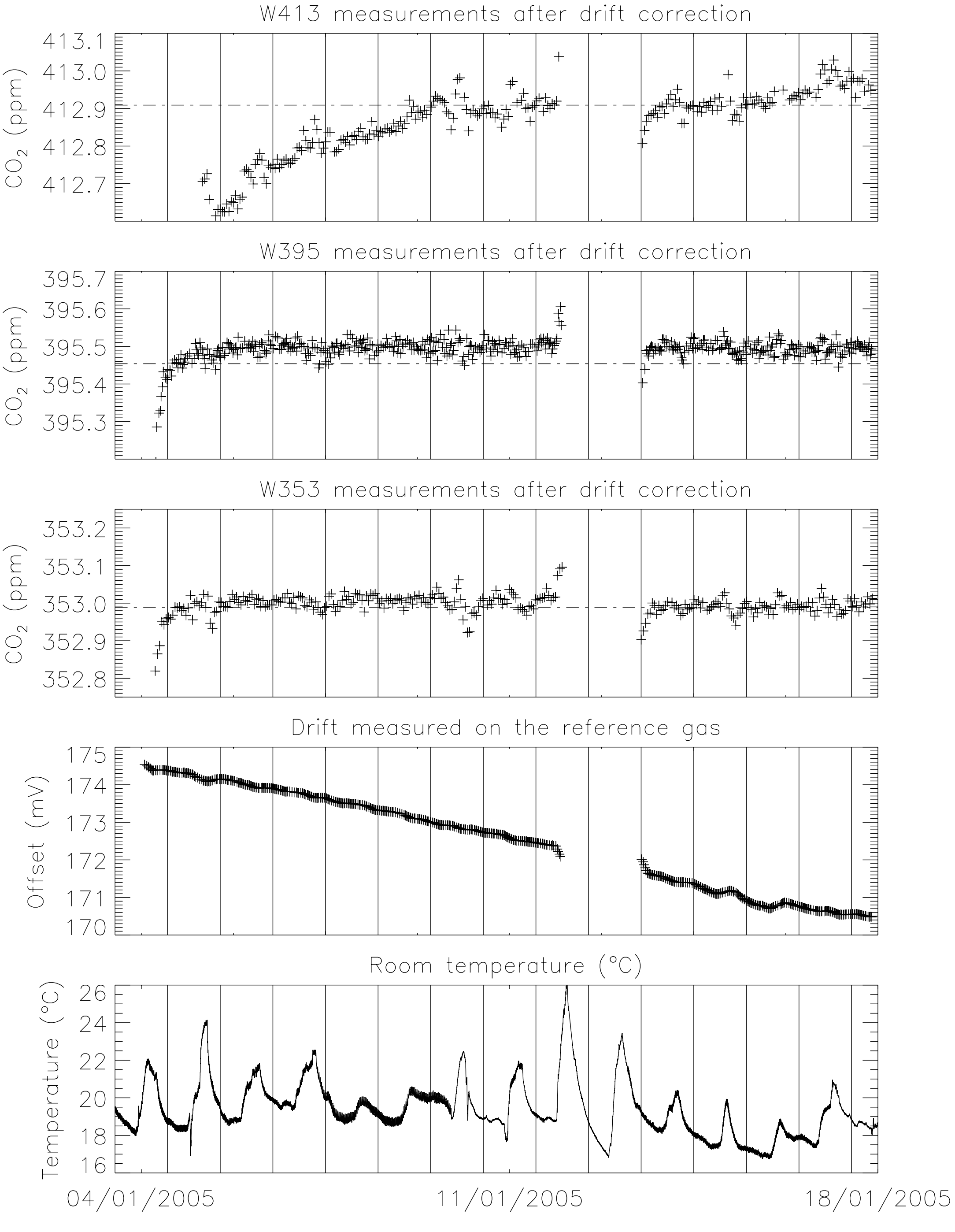

Figure 6: **Example of CARIBOU laboratory measurements. The 2-weeks reproducibility after a simple drift correction obtained by measuring the reference gas, and using only one initial calibration, is about 0.02 ppm rms.**

The preliminary performance results obtained in the laboratory are given in Table 1:

Table 1: **List of CARIBOU preliminary laboratory performance.**

Licor Cell pressure regulation	< 10 µbar rms
Thermal regulation	5 mK rms
Gas flow regulation	1.5 µl/min rms
Reproducibility of standard gas (preliminary)	0.02 ppm rms
Typical residual drift after drift correction	1 ppb/day

At the field sites, the calibration of the full span of the instrument is done every 8 days using up to 6 standard gases with a concentration range of 340-450 ppm. We repeat a pyramid-like pattern several times, flowing the calibration gases and the reference gas in ascending and descending order of concentrations; each standard gas analysis lasts 10 minutes. For the following calculations, a mean of the last 6 minutes of analysis is taken.

To determine and correct the instrument drift, the reference gas is injected for 10 min in the sample cell one time per hour. After this drift correction, the laboratory results showed that the residual drift is as low as 1 ppb per day, which allows the calibrations of the instrument to be done no more frequently than once every 8 days to maintain the goal for precision of 0.01 ppm. Finally, for quality control, a target gas is injected every 13 hours. All the data processing applied to the air measurements is also applied to the target gas measurements, allowing for monitoring of the instrument performance and long-term stability.

As an example of *in situ* data, Figure 7 shows the CO_2 continuous measurements at Biscarrosse during the Carboeurope Intensive Regional experiment. We are now refining the details of the calibration protocol (number of calibration pyramids, number of standard gases really needed, etc.) in the field, which have less stable environmental conditions than in the lab (for example, drastic diurnal temperature change inside the tower at Biscarrosse).

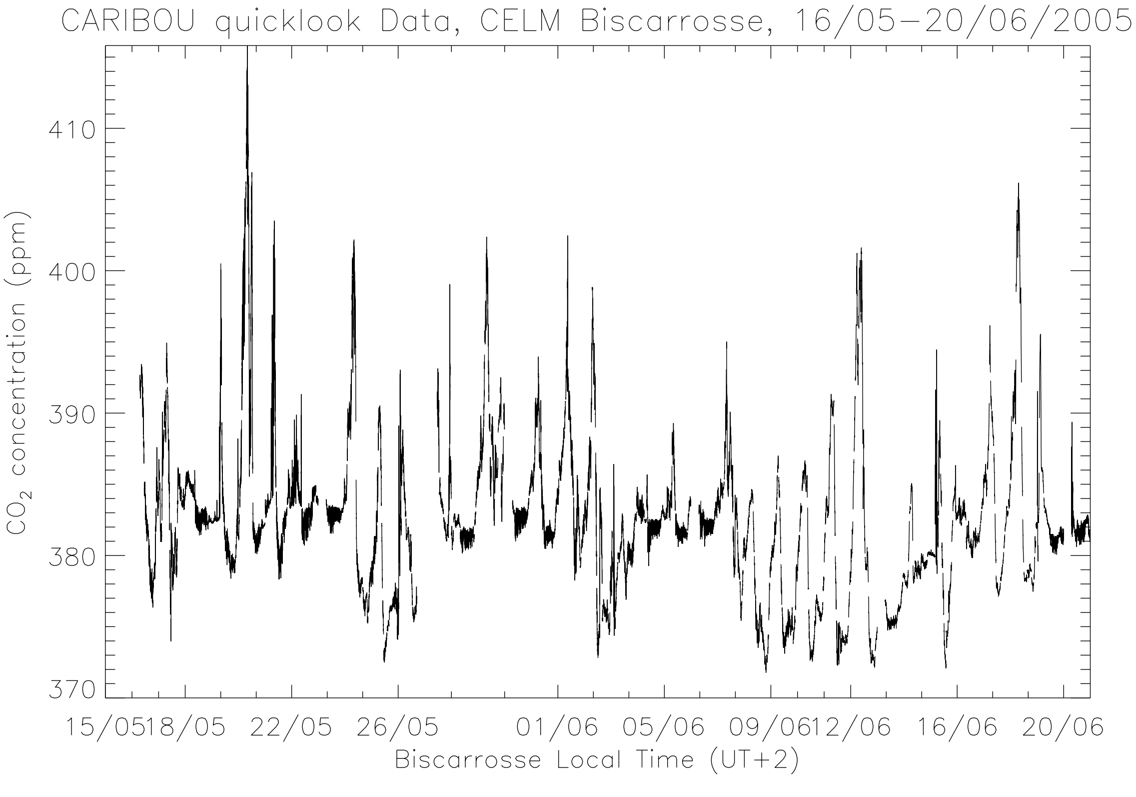

Figure 7: **Example of CARIBOU measurements: CO_2 series at Biscarrosse, France.**

3.1.5 Conclusion

LSCE and DAPNIA/SIS have developed and started the implementation of a new high-precision continuous CO_2 monitoring network. The low gas consumption, the high hardware reliability, as well as the automation of data transfer and the implementation of automatic alarm messages, should allow minimizing the required maintenance manpower. The performance obtained in the laboratory is very promising and will have to be confirmed at the various sites.

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3.2 Performance of the LoFlo Continuous CO_2 Analyser: Baseline and Urban Air Monitoring; Diagnostic Capability, and Potential for Enhanced CO_2 Calibration

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3.2.1 Introduction

The CSIRO-developed *LoFlo CO_2 Analyser* is a high precision and continuous atmospheric CO_2 analysis system[1]. Compared to conventional systems it exhibits improvements in measurement precision, at the same time reducing consumables and the requirement for operator intervention. There is potential for the system to greatly improve atmospheric monitoring traceability and network comparability[2].

The LoFlo system has been deployed at a number of atmospheric global monitoring sites and supporting laboratories around the world (Figure 1). In the CSIRO programme, a LoFlo system at Cape Grim Baseline Air Pollution Station (BAPS) is the central element in a planned Southern Ocean regional CO_2 network. This network is being established to resolve the small atmospheric CO_2 spatial gradients and the possible changes of CO_2 fluxes in this important region[3].

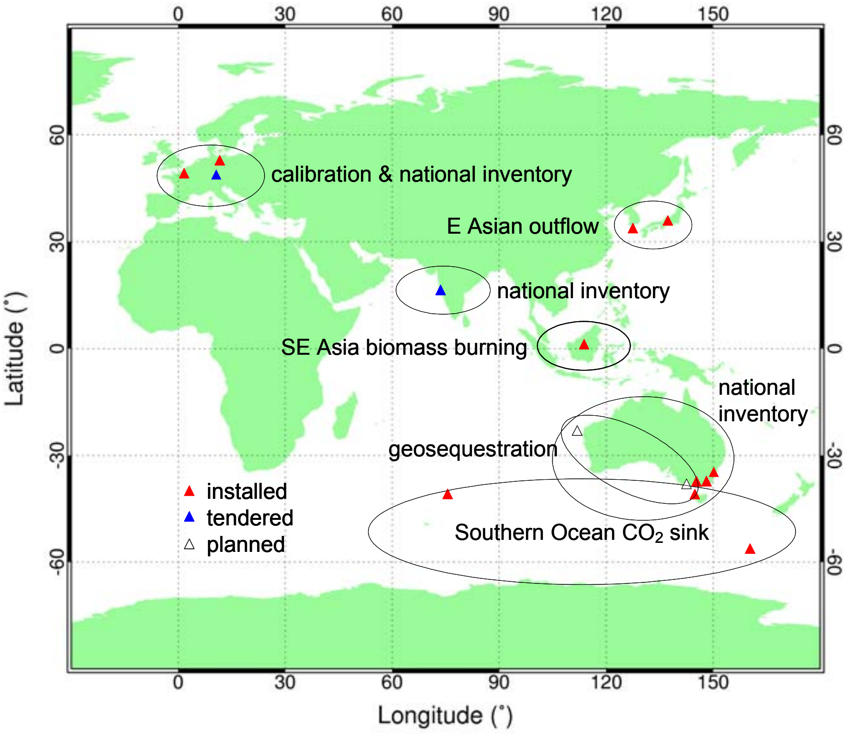

Figure 1: The expanding global LoFlo analyser network.

To meet the challenge of monitoring small differences between southern ocean sites (as well as other sites around the world), the intrinsic high precision of the LoFlo air monitoring system needs to be combined with CO_2 standards-calibration-accuracy at the same level of high precision, which is not yet achievable via current international CO_2 standards[4,5].

3.2.2 LoFlo High Precision Performance for Baseline Air Monitoring Networks

A prototype LoFlo analyser has been operating at Cape Grim BAPS since May 2000, with the current second generation model operating there since April 2004.

An “overlap” experiment was conducted at Cape Grim BAPS (July to August 2005), involving two individually calibrated LoFlo analysers (identified here as LoFlo 2A and LoFlo 2B, each one operating with its own suite of calibration gases). The seven high-pressure, CO_2-in-dry air calibration standards used for LoFlo 2B were calibrated at the WMO Central CO_2 Calibration laboratory at NOAA CMDL[4]. The seven-cylinder calibration suite of LoFlo 2A was calibrated intensively against the LoFlo 2B calibration suite.

The analysers continuously monitored marine boundary layer air from a shared single air intake. The results are portrayed in Figure 2.

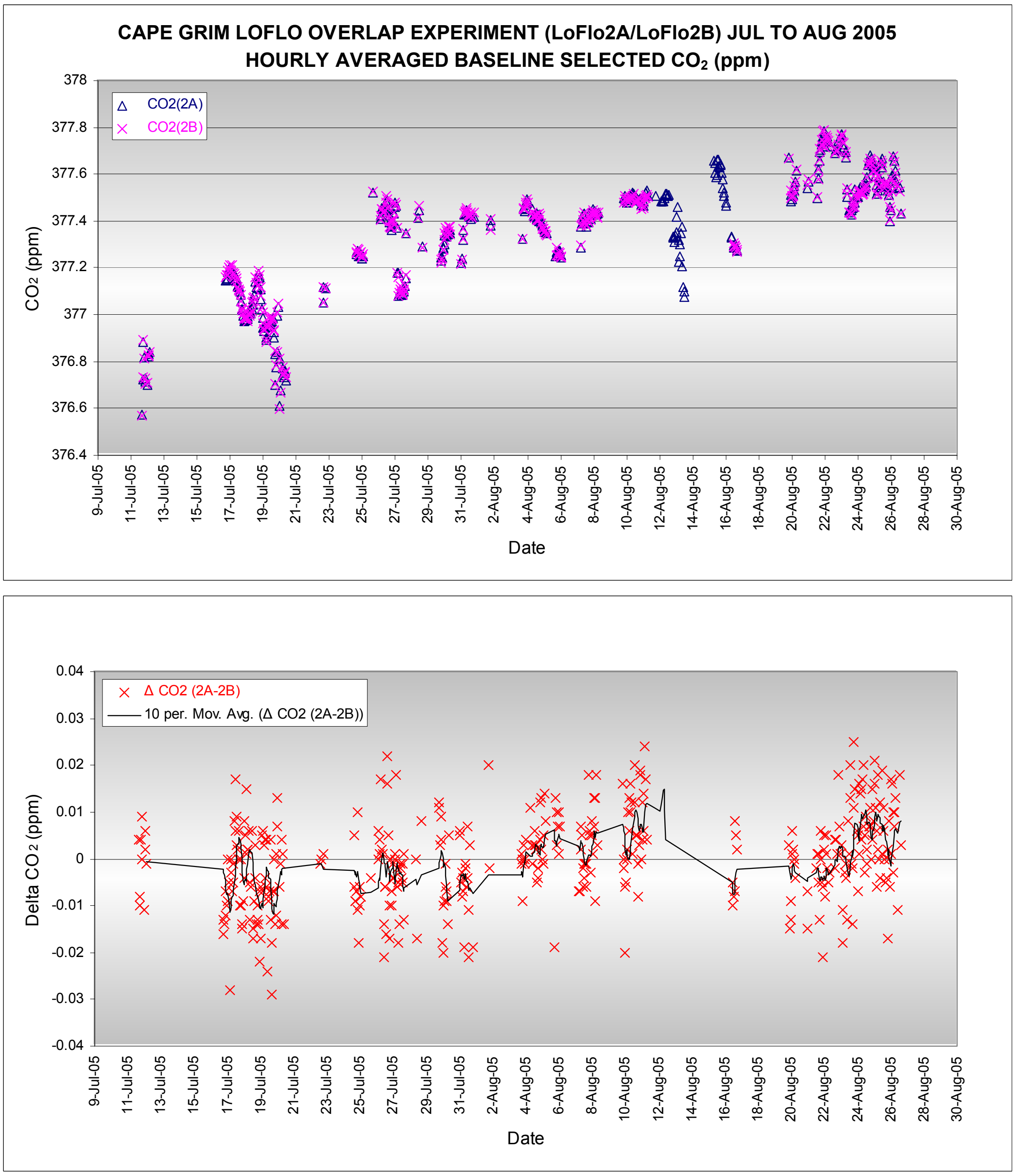

Figure 2: **Dual LoFlo Air Monitoring Experiment (Cape Grim, hourly averaged CO_2). Top panel shows absolute values and bottom panel shows differences between the analysers.**

The results demonstrate very good agreement between the two instruments with a mean difference of 0.000 ± 0.010 ppm CO_2. The differences in individual hours exceed the repeatability of measurements on a constant source (high pressure cylinder of air) and are not yet fully understood. Another concern is the impact of possible error (at their specified 0.06-0.1 ppm level) in the original NOAA assignments. However, the overall result is highly encouraging, and supports an expectation that it will be possible to propagate a central calibration scale with improved precision.

As a step in this direction, we propose to introduce a circulator suite of three small volume pressurised gas cylinders (spanning a suitable CO_2 concentration range), each with dedicated pressure regulators. These components will all be contained in a single standard sized suitcase for ease of shipment between users. The initial aim will be to monitor differences between independently calibrated and operated LoFlo systems and confirm that differences over interannual timescales are within the required high precision.

3.2.3 Enhanced LoFlo Precision

The LoFlo measurement strategy utilises very precise gas flow and pressure control, incorporating the highest quality sensors available. The *Baratron* (MKS, Type 223) differential pressure sensor allows precise measurement of the difference in pressure (DP) between the sample and reference cells of the Li-Cor IR sensor in the LoFlo. Currently the DP sensors readings are recorded (every 1 second) and averaged over 1-minute periods. There remains a well defined relationship between DP and recorded CO_2 output from the Li-Cor (Figure 3).

This observation has prompted work to further enhance the analytical precision of the LoFlo significantly by applying an initial DP correction for each 1-second CO_2 Li-Cor output, prior to minute averaging data processing.

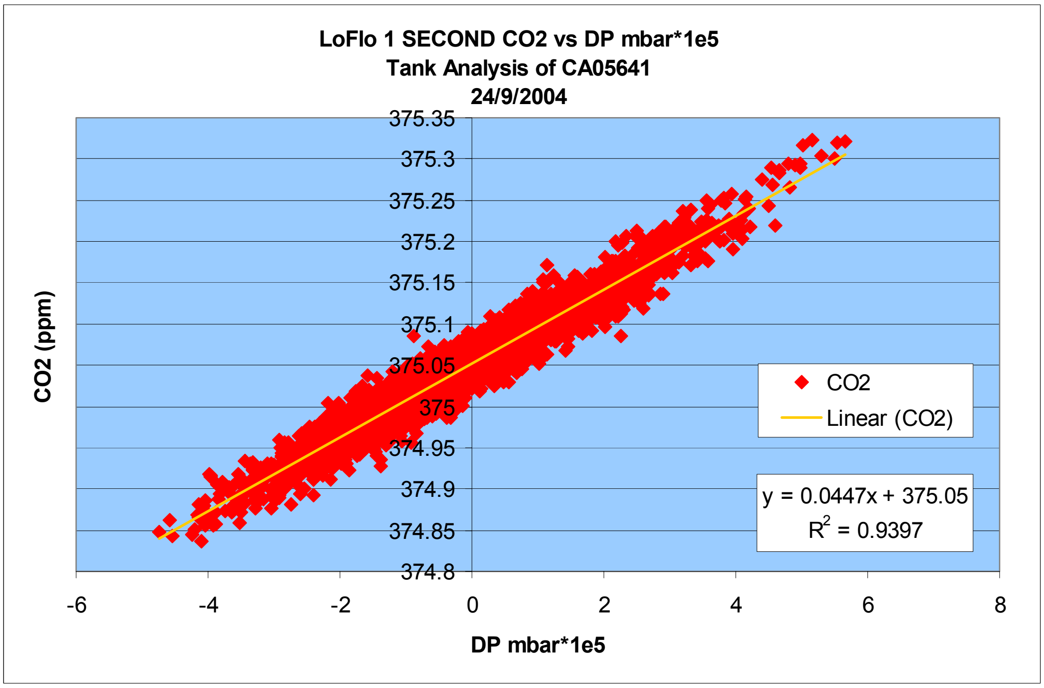

Figure 3: **CO_2 correlation with differential pressure between reference and sample Li-Cor cells.**

3.2.4 LoFlo High Precision Performance for Enhanced CO_2 Calibration

The high precision and stability of the LoFlo enhances its diagnostic potential in detecting even very small drifts in CO_2-in-air calibration standards, in addition to temporary biases introduced by surface adsorption effects, most likely in the pressure-reducing regulators, which often interfere with precision calibration.

The calibration history of LoFlo2B system reveals the outstanding consistency of the repeat measurements of cylinder air over an extended period. This is shown by plotting the calibration residuals (assigned CO_2 minus quadratic fit CO_2) from each calibration event for each of the seven calibration cylinders (Figure 4). The shaded section shows irregularity, which corresponds to an interruption to continuous operation, after the LoFlo was moved from Aspendale to Cape Grim.

This diagnostic test is useful for the early identification of relative drifts in calibration cylinders and/or regulator effects.

Assuming a smooth quadratic fit to the infrared response of the Li-Cor analyser, the value of each of the residuals will also reflect uncertainty in the original CO_2 calibration assignments, and will quantitatively measure changes in cylinder composition once the original assignments are made with comparable precision.

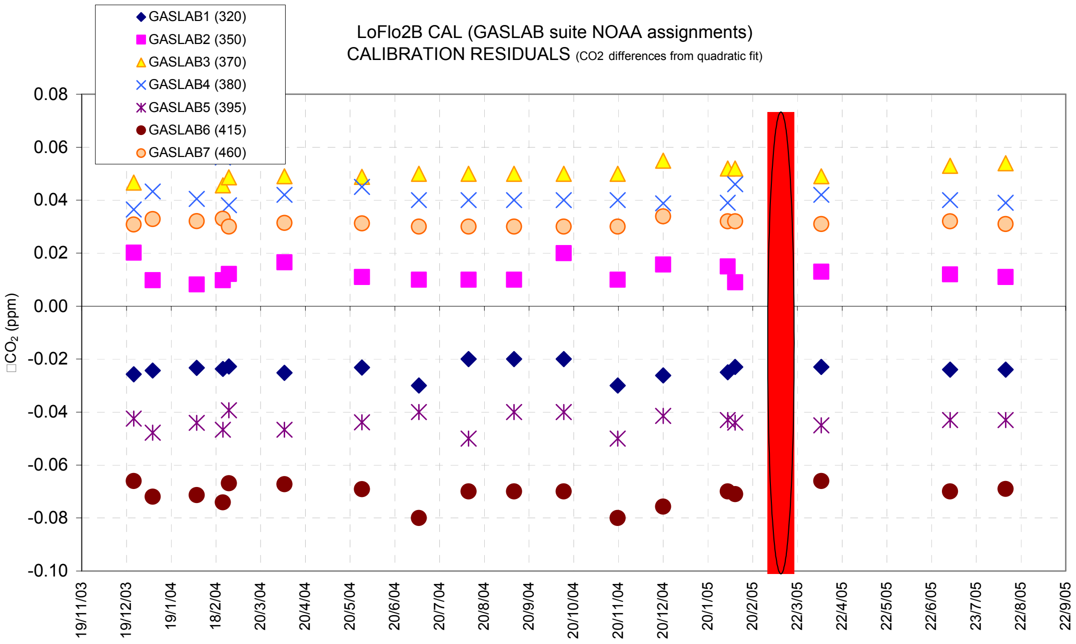

Figure 4: **LoFlo calibration residuals (assigned CO_2 – quadratic fit CO_2) history.**

3.2.5 Conclusions

The features of the LoFlo atmospheric CO_2 analysis system are being used most effectively in applications such as:

- Air monitoring where high precision measurement is important (e.g. Southern Ocean region).
- Air monitoring where logistic support (consumables and operator intervention) is limited (Tumbarumba forest site; Amsterdam Island; Danum Valley, Malaysia, Mt. Fuji, Japan; Gosan Island, Korea).
- Diagnostics for CO_2 measurement (Australia National Measurement Institute, CSIRO-CMAR; LSCE, France; MPI, Germany).
- Atmospheric profiling experiments for virtual tall tower applications.
- Propagation of measurement scales from central laboratory to field sites and campaigns (LSCE, France; CSIRO-CMAR; MPI, Germany).

Tests outlined here have demonstrated the stability and repeatability of the LoFlo anaylsis system. Significantly, tests on the comparability of air measurements from two individual analysis systems that are linked using propagated calibration scales (from a parent calibration suite) and sharing the same air intake, shows encouraging results.

In addition, opportunities to further improve the LoFlo precision are being implemented.

Acknowledgements

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3.3 An Autonomous Inexpensive Robust CO_2 Analyzer (AIRCOA)

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3.3.1 Introduction

We present our design of a new autonomous, inexpensive, and robust CO_2 analyzer (AIRCOA), a description of our quality control procedures, and data examples from ongoing deployments. Our AIRCOA units require less than $10K (US) in components, can be assembled and tested in 4 weeks or less, show intercomparability of 0.1 ppm or better during laboratory and field tests, and run autonomously for months at a time.

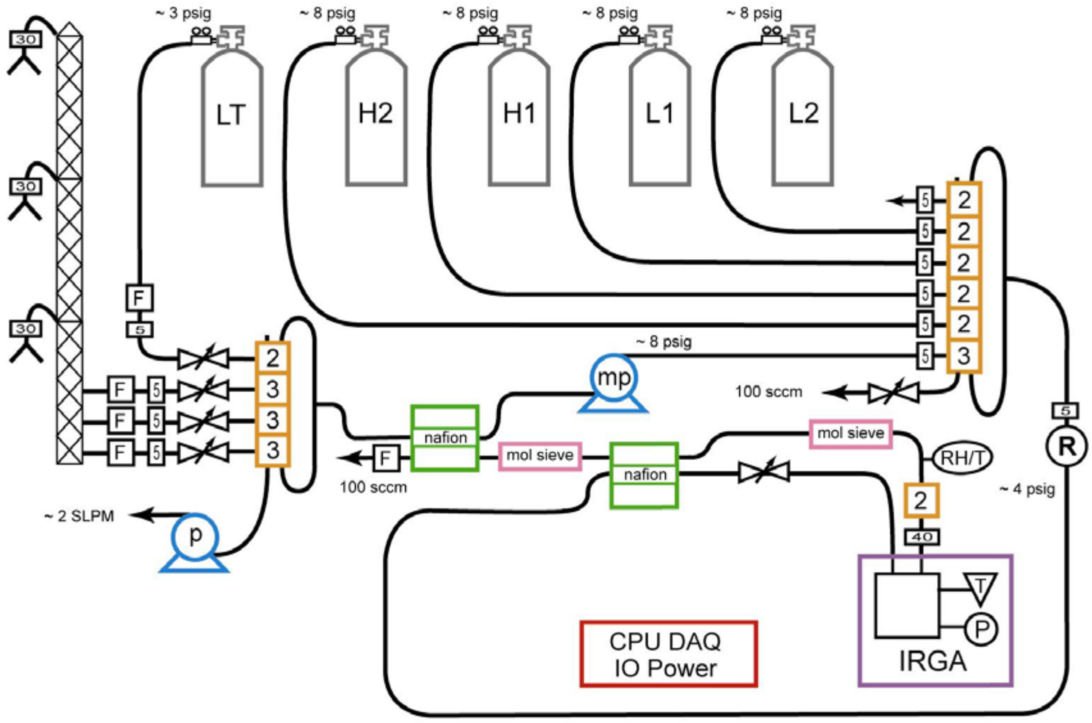

Figure 1: **Schematic showing the AIRCOA design. Components include three sample air intakes with rain shields and 30 μm filters (30), mass-flow meters (F), 5 μm filters (5), manual needle valves, three-way (3) and two-way (2) solenoid valves and manifolds, Nafion driers, molecular sieve driers, a sample micropump (mp) and purge pump (p), four reference cylinders, one surveillance cylinder, two-stage pressure regulators, a single-stage pressure regulator (R), a humidity and temperature sensor (RH/T), a PC104 computer running Linux, PC104 relay and A/D boards, a power supply, and a LiCor 820 single-cell IRGA.**

There is a strong motivation to improve atmospheric carbon flux constraints from continental scales (~10,000 km) to regional scales (~1000 km) so that they can be better related to the underlying ecosystem processes, land-use histories, and climate forcing. This requires a considerable increase in the temporal and spatial density of accurate atmospheric CO_2 observations, which would be significantly aided by lowered costs and improved reliability of continuous CO_2 analysis systems. As part of the Carbon in the Mountains Experiment (CME), we developed AIRCOA for the purpose of observing local scale CO_2 gradients across a network of towers at the Niwot Ridge carbon flux site, and have since begun deploying the same system in a regional CO_2 observing network.

Making accurate CO_2 measurements requires careful attention to gas handling, numerous automated quality control diagnostics, and a suite of reference cylinders closely linked to the WMO CO_2 calibration scale. Our approach builds on those of Zhao et al. (1997) and Trivett and Köhler (1999), but with considerable changes (see Figure 1). AIRCOA is based on a single-cell infrared gas analyzer (IRGA), which dramatically lowers the cost but increases the short-term noise and instrument drift rate. We overcome the short-term noise with signal averaging and instrument drift with frequent calibrations. Additional potential sources of CO_2 measurement bias that we address with automated diagnostics include: incomplete flushing of the sample cell and dead volumes, incomplete drying of the sample air, IRGA sensitivity to pressure broadening, IRGA sensitivity to temperature, leaks to ambient air, leaks of calibration gas through solenoid valves, and modification of CO_2 mixing ratio by the drying system or plastic components (see Table 1).

3.3.2 Instrument Design

As shown in Figure 1, we sample air from three heights on a tower, using inlets consisting of rain shields, and quartz wool and 30 μm polypropylene filters. The instrument box is generally indoors in an environment with moderate temperature variability, but in principle it could also be outdoors. Each inlet stream passes through a mass-flow meter (Honeywell, AWM3000V), and a 5 μm metal filter and needle valve (Beswick Engineering, CF and MLS series) before reaching a manifold of solenoid valves (Numatech, TM10 series). A brushless DC diaphragm pump (KNF Neuberger, N89) flushes the sample lines at 500 to 1000 sccm when they are not being analyzed. The one gas selected by these valves exits through both ends of the manifold and then passes through the first of two 2.44 m by 2.8 mm ID Nafion driers (Permapure, MD series). A smaller brushless DC diaphragm pump (KNF Neuberger, NMP015B) then compresses this gas to approximately 55 kPa above ambient at which point it passes through a second 5 μm metal filter and enters a second solenoid valve manifold.

Table 1: Potential sources of measurement error and AIRCOA solutions.

Measurement Concern	Solution
Short-term IRGA noise	Average for 100 seconds to get 0.1 ppm precision
Incomplete drying of air	Slow flow; two 2.44 m Nafion driers; downstream humidity sensor to verify
Incomplete flushing of cell	Sufficient flow; alternate calibration sequence low-to-high / high-to-low
Drift in IRGA sensitivity	4-hourly 4-point calibrations and 30-minute 1-point calibrations
Inadequate IRGA pressure calibration	Automated 4-hourly pressure sensitivity measurements
Leaks through fittings and valves	Automated 8-hourly positive pressure and 4-hourly ambient pressure checks
Temperature sensitivity of IRGA	Empirical temperature sensitivity correction from 30-minute 1-point calibrations
Drying system affecting CO_2	Constant flows, pressures, and humidity in Nafions; CO_2 in Nafion purge air
Other plastics affecting CO_2	Minimize changes in pressure drop at inlet
Different sensitivity with and without Ar	Use calibration gases made with real air
Fossil CO_2 in calibration gases	Comparisons to laboratory Siemens Ultramat 6F limit ^{13}C effect to 0.05 ppm
Regulator temperature effects	Laboratory tests show effect to be negligible; monitor for anomalous regulators
System diagnostics and verification	8-hourly analyses of surveillance gas run through entire inlet/drying system
Links to WMO scale	Laboratory calibration transfer facility; comparison to GMD flasks at NWR
Development of problems in the field	Near real-time data retrieval, processing, diagnostic checking, and display

This second manifold selects either a sample gas or a calibration gas to be analyzed. When the sample gas is not being analyzed it exits the valve manifold through a needle valve set to maintain constant pressure in the upstream Nafion drier. The four calibration gases typically span the range 340 to 480 ppm and are stored in high-pressure aluminium cylinders with Ceodeux valves (Scott Marrin Inc.) and two-stage brass regulators (Scott Specialty, model 14). These regulators are set to match the pressure in the sample line. We use 10 L high-pressure cylinders which last 12 months at our flow rates and calibration frequency. A fifth calibrated high-pressure cylinder stores a long-term surveillance gas which we run through the entire inlet system and treat as an unknown during analysis. The regulator on this cylinder is set to approximately 21 kPa above ambient and a needle valve is used to match sample pressures in the first Nafion drier.

The sample or calibration gas selected for analysis next passes through another 5 μm filter and a miniature pressure regulator (Beswick Engineering, PRD series) with an output of approximately 28 kPa above ambient. The gas is then dried by a second Nafion drier and reduced in pressure by a needle-valve (Swagelok, S series) before reaching a single-cell IRGA (LiCor, Li820). We adjust this needle valve to set the sample flow to 100 sccm. After leaving the IRGA, the gas passes through a 40 μm metal filter, a normally-open needle valve used for leak checking purposes, and a humidity and temperature sensor (Vaisala, HUMITTER 50Y) used to verify drier performance. We then completely dry the gas once with molecular sieve 13X to use it as the purge gas on the second Nafion drier, and dry it a second time to use it as the purge gas on the first Nafion drier. Most of the moisture in the ambient air exits the first Nafion without ever reaching the molecular sieve driers. We use 200 ml molecular sieve driers which last 6 to 12 months depending on outside humidity. The gas passes through a final mass-flow meter before exhausting to the room. There is little flow impedance between the Li820 cell and this exhaust such that sample and calibration measurements are both closely matched to ambient pressure.

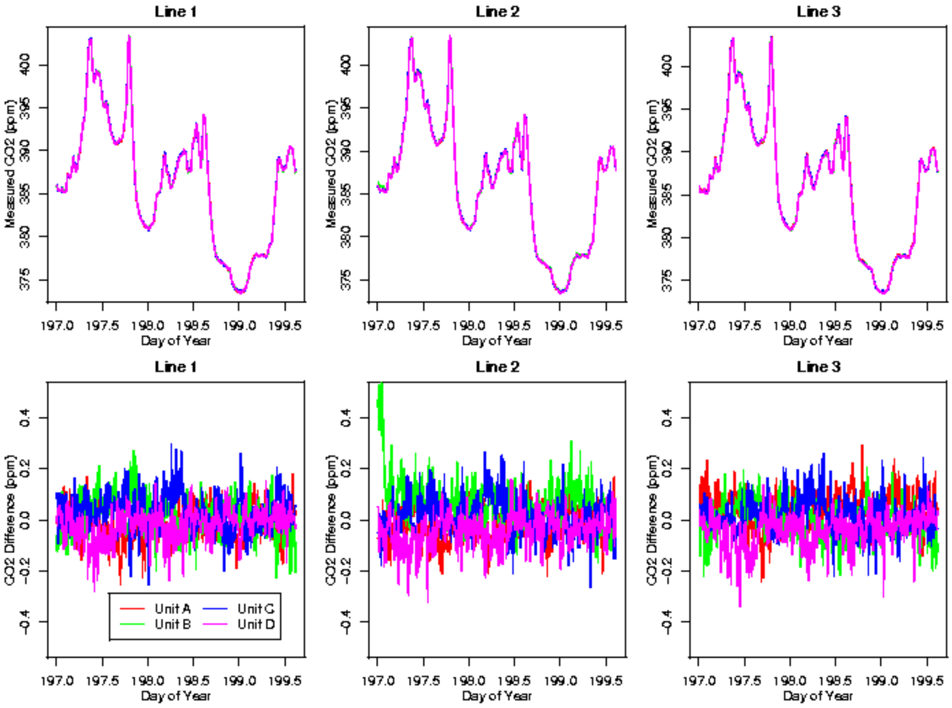

Figure 2: **Measurements (top panels) made by 4 AIRCOA units on 3 days in Broomfield, CO during July 2005. These units were all in a laboratory with their inlet lines connected to a common manifold sampling outside air and common calibration cylinders. Comparison of measurements made by each unit during this period (bottom panels) shown as differences from the 4-unit median value at each sample time. The means (and 1-sigma standard deviations) for the 6 pair-wise differences were 0.05 (0.13) ppm or better.**

The Li820 measures the pressure, temperature, and CO$_2$ mixing ratio of the gas. It actively and precisely controls the optical bench to 50 ˚C and has excellent stability with respect to ambient temperature of around 0.05 ppm/°C, which is a factor of 10 better than more expensive LiCor analyzers. We set the Li820 to use a 0.5 Hz digital filter and report values at 1 Hz. These filtered values have a 1-sigma rms noise of 0.6 ppm which averages to 0.1 ppm over 100 seconds. We switch the gas being analyzed every 150 seconds and ignore the first 50 seconds after each switch to allow for flushing of gases through the system. We then cycle between the three inlet lines on a 7.5 minute schedule. We make a calculation based on measured flows of how long the measured gas takes to get from the inlet to the sample cell and adjust the times of our reported measurements accordingly. Every 30 minutes we analyze one of the 4 calibration gases to estimate drift in the Li820 zero offset, while every 4 hours we measure all four calibration gases to estimate linear and 2nd-order calibration coefficients for the Li820. We alternate the sequence of these 4 gases to look for problems associated with incomplete flushing of the sample cell and any dead volumes. Every 8 hours we analyze the long-term surveillance gas.

Every 4 hours we also perform automated system checks to determine the Li820 pressure sensitivity and to measure system leak rates to ambient at positive pressure and from the solenoid valves at ambient pressure. We make considerable efforts to minimize and monitor system leaks. Because of silicone seals in the Li820, plastic fittings on the Nafion driers, viton seals in the solenoid valves and manifolds, and plastic and viton seals in the micropump it is not practical to completely eliminate them. A leak of calibration gas with a 100 ppm difference from sample air through the solenoid valves at a rate of 0.1 sccm would result in a 0.1 ppm bias in our measurements. We set an operational target of 0.015 sccm for the total of all solenoid valve leaks and an absolute data-rejection cutoff of 0.03 sccm. It is more difficult to estimate the effect of positive-pressure leaks to ambient, but because of the potential for diffusion against flow they are not negligible. We test at 5 kPa overpressure and use the same target and cutoff rates as for the ambient leak-up test.

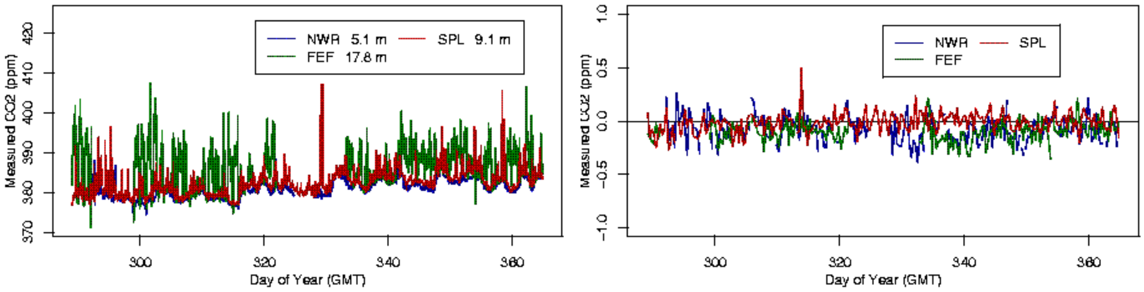

Figure 3: **Measurements (left) made by 3 AIRCOA units from October 16 through December 30, 2005 in the field in Colorado: at Niwot Ridge (NWR), at Fraser Experimental Forest (FEF), and at Storm Peak Laboratory (SPL). Only values from the highest intake lines at these sites are shown. Comparison of surveillance cylinder measurements (right) made by each unit during this period, shown as differences from their laboratory assigned values. The means (and 1-sigma standard deviations) of these differences were -0.08 (0.13), 0.10 (0.10), and -0.01 (0.10) ppm respectively.**

A PC104-based computer running Linux performs automated data acquisition and valve control. We access this system through a dedicated internet connection and retrieve, process, and display data and system diagnostics in near real time. If any of the automated diagnostics suggest a problem, we are then able to perform more detailed troubleshooting interactively. We cannot overstress the value of this direct connectivity and rapid processing for maintaining the systems and producing high-quality CO_2 measurements.

3.3.3 Results

In a week-long laboratory inter-comparison between 4 AIRCOA units all sampling outside air from a common mixing volume and using common reference cylinders, unit-to-unit differences on coincident measurements showed 1-sigma variability of 0.13 ppm and systematic biases of 0.05 ppm or less (see Figure 2). During isolated field operation comparability is more difficult to assess, but we use 8-hourly analyses of surveillance tanks to estimate performance. We installed three AIRCOA systems in the field at the start of September 2005. Despite the added complexity of different sets of calibration gases and larger temperature variations in comparison to the laboratory tests, the units still perform very well. While periods of systematic bias of up to 0.2 ppm are evident, averaged over a period of 2.5 months the 1-sigma variability for these three units ranged from 0.10 to 0.13 ppm and the systematic bias ranged from 0.01 to 0.10 ppm (see Figure 3). This figure also illustrates that the systems have been operating with relatively few data gaps during their initial deployments. We are working closely with other investigators developing and deploying similar single-cell IRGA based systems, as well as investigators deploying longer-established but more expensive technologies, in an effort to improve the inter-comparability between independent observing networks.

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3.4 A New Quantum-Cascade Laser Based Spectrometer for High-Precision Airborne CO_2 Measurements

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Abstract

We present a new, compact, fast response (1 Hz) mid-IR laser spectrometer for high-precision airborne measurements of CO_2. The instrument uses a thermoelectric-cooled, pulsed-operated distributed feedback (DFB) quantum-cascade laser (QCL). Unlike conventional cryogenically-cooled continuous wave (CW) Pb-salt diode lasers, QC lasers display high mode purity and wavelength stability, and can be operated at near room temperature. This last attribute allows for a compact design and simplified operation.

The CO_2 mixing ratio is derived from direct absorption spectra obtained by electrical modulation at 9 kHz of the laser wavelength across a selected υ_3-band transition at around 4.32 µm. The measurements are thus fully specific of the CO_2 molecule and free from interference of H_2O or other mid-IR light absorbers. Sample gas humidity is nevertheless reduced to less than ~300 ppm in order to restrain density variation effects.

Absorption spectra of the sample and a flowing standard (reference) along a 10-cm (or 5-cm) path are simultaneously measured with LN_2-cooled InSb detectors. The CO_2 mixing ratio difference is retrieved from the differential spectrum (sample/reference). The advantages of this "null" mode operation are discussed in detail below.

The spectrometer is enclosed in a temperature controlled, hermetically sealed vessel. The enclosure is flushed with CO_2-free dry air previous to operation in order to avoid light absorption in the external path.

The demonstrated short-term precision of the instrument is better than ~50 $\text{ppb}\cdot\text{Hz}^{-1/2}$ (1-sigma in 1-s integration time) for CO_2 mixing ratios within ±50 ppm of the reference mixing ratio. An accuracy of ±0.1 ppm or better is insured through periodic calibration with high, low and long-term surveillance standards traceable to NOAA/ESRL.

3.4.1 Rationale

The quantification of regional to continental scale CO_2 sources and sinks based on inverse modelling techniques [Lin, 2003] requires CO_2 measurements traceable to world standards to ±0.1 ppm or better [Gerbig, 2003]. In a similar way, the precision achieved on the definition of the transport rates in the stratosphere [Andrews, 1999; Boering, 1996] and the tropical tropopause layer based on airborne CO_2 measurements is directly proportional to the instrument precision and traceability.

Non-dispersive infrared (NDIR) CO_2 instruments developed at Harvard University have demonstrated short-term precisions of better than ±50 ppb, and flight-to-flight precisions and traceability to NOAA/ESRL standards typically to better than ±0.1 ppm for over 400 flights, including balloon borne measurements up to 32 km altitude [Daube, 2002]. This stability has been achieved through tight control of temperatures, pressures and sample humidity, and careful calibration. This is necessary partially because of the strong, non-linear temperature and pressure dependences of the absorption band cross section used by the NDIR technique. First demonstrated in 1994 [Faist, 1994], and rapidly developed thereafter [Gmachl, 2001], QCLs are today a practical laser alternative to thermal (broadband) light sources for spectroscopic measurement of CO_2 in the mid-IR.

3.4.2 Spectroscopic and QCL Management Considerations

NDIR CO_2 instruments are based on single or dual channel measurement of the absorption of broadband, incoherent light (e.g. from a tungsten filament lamp) by almost the entire CO_2 υ_3 band (see Figure 1). Unlike them, the CO_2 QCL spectrometer operates by resolving the absorption spectrum of a single (or reduced number of) CO_2 υ_3 transition(s) over a spectral microwindow.

The strongest CO_2 band (υ_3 – asymmetric stretch) provides enough absorption for precise measurements over short absorption pathlengths (5-10 cm). The optimum υ_3 transition is the one with the minimum temperature dependence rather than the one with the highest linestrength. We have identified this transition as the moderate energy state P(34) line at 2319.18 cm^{-1}. This line has a relative temperature dependence of $\sim 10^{-6}$ K^{-1}, and the fundamental lines around also have a lower temperature derivative compared to their counterparts in the R branch.

We have only recently procured QC lasers capable of reaching this wavelength. We initially performed measurements at 2311.10 cm^{-1} and 2313.16 cm^{-1}, including isotopic $^{13}CO_2/^{12}CO_2$ measurements on a modified dual QCL spectrometer [McManus, 2005; Saleska, 2006].

Our measurements are based on direct absorption (rather than derivative) spectroscopy with single mode, mode-hop free, thermo-electrically cooled (TEC), DFB InGaAs-InAlAs/InP QC lasers (Alpes Lasers). We pulse them at low duty cycles (~1.2%) near threshold, and with the shortest possible electrical pulses necessary to build coherence (~12 ns FWHM), in order to minimize spectral chirping (proportional to electrical pulse length and voltage above threshold). The resulting QCL linewidths are typically $\sim 10^{-2}$ cm^{-1} HWHM. Pulsed operation results in high mode purity near threshold, a simpler and more robust TEC-based operation, and is intrinsically less affected by interference fringes due to its shorter coherence length (compared to CW laser operation) enhanced by gated detection. The QCL linewidth sets the optimum operation pressure at ~70 hPa, pressure at which QC lasers and Voigt-broadened molecular transitions have comparable linewidths.

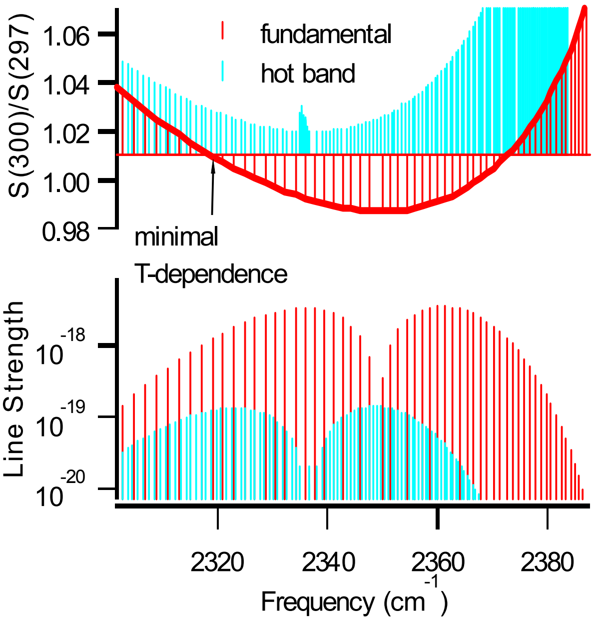

Figure 1: **Linestrength (lower panel) and linestrength temperature derivative (upper panel) of the fundamental (υ_3 – red) and hot bands (blue) of CO_2 around 2350 cm^{-1}(~4.3 µm). CO_2 NDIR instruments measure absorption over a ~80 cm^{-1} window centered at ~2350 cm^{-1}.**

Molecular transition selection for a given QCL is achieved by temperature tuning within –40 °C and +40 °C using a two-stage Peltier module. The available spectral range (~14 cm^{-1}) is entirely determined by the temperature dependence of the waveguide (DFB) refractive index ($\sim 7\times 10^{-5}$ K^{-1}) [Hofstetter, 2001]. We keep a laser sink temperature stability of better than 1 $mK\cdot Hz^{-1/2}$ using compact, commercial controllers.

Direct absorption spectra are obtained by repetitively pulsing the QCL (1 MHz) while simultaneously modulating the QCL wavelength by applying a sub-threshold current ramp (9 kHz) that raises the QCL temperature (a ~50 mA ramp typically causes a ~3 K temperature increase, which sweeps the laser wavelength over ~0.3 cm^{-1} – see Figure 2).

The spectral range is optimized for precision with most of the sweep occupied by the core of the absorption transition rather than by its spectral baseline. The penalty on accuracy is only apparent as the present accuracy of the HITRAN spectral database parameters [Rothman, 2003]; this, along with the imperfect knowledge of the actual QCL lineshape, impedes retrieving mixing ratios accurate enough for CO_2 (direct retrieval typically underestimates calibrated mixing ratios by 5% or less). In order to insure accuracy, we instead do frequent zeroing (~4-6 hr^{-1}) and frequent calibration with low- and high-span gases (~2-4 hr^{-1}), and sparingly with long-term surveillance standards (~0.5 hr^{-1}), all calibrated against the WMO CO_2 scale (maintained by NOAA/ESRL).

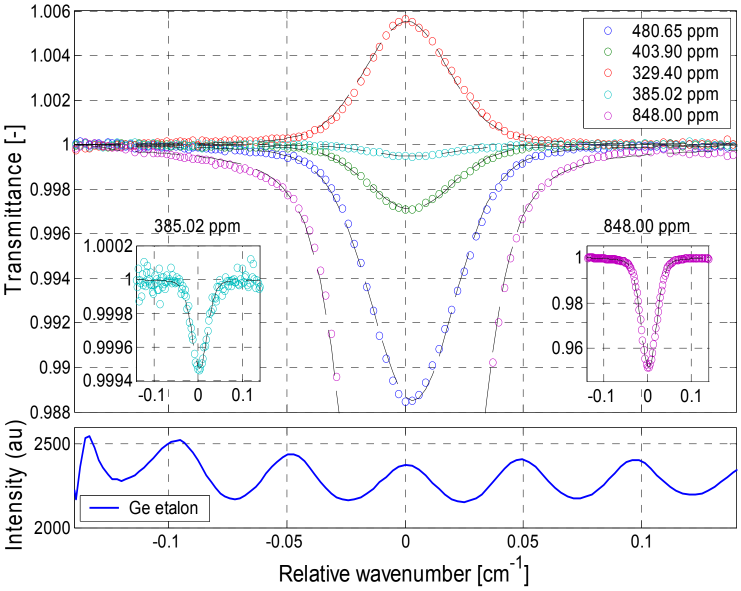

Figure 2: **1-Hz QCL differential absorption spectra of the CO_2 υ_3 P(40) line (2313.16 cm^{-1}) at various calibration tank concentrations relative to a 378.30 ppm reference. The lower panel shows the tuning rate (25-mm Ge etalon spectrum). The dashed lines are real-time calculated non-linear fits. Residuals are typically ~2×10^{-4} p-p optical thickness.**

A basic feature of the CO_2 QCL spectrometer is the simultaneous measurement of sample and reference absorption spectra (dual beam). The spectrometer operation in "null" mode (sample/reference) has several benefits: (1) Eliminates the effect of pulse-to-pulse (and sweep-to-sweep) variations by normalization (covariance subtraction); (2) Reduces the impact of variations of temperature, laser linewidth and centre wavelength (drift); (3) Cancels to large extent interference fringes produced in the absorption cell and in the external path (matched to better than ~5%); (4) Increased accuracy at mixing ratios near that of the reference gas (free troposphere ≈ 380 ppm); (5) The differential spectrum is optically thinner and its baseline is better defined than either the sample or the reference spectra, which renders improved linearity and accuracy, respectively.

3.4.3 Airborne Spectrometer

The optical table is shown in Figure 3. The divergent QCL beam is focused using a 13 mm ϕ aspheric ZnSe lens and then split into sample (reflected) and reference (transmitted) beams using a CaF_2 beam splitter. After a single pass through a 10-cm (or 5-cm) long dual absorption cell, the beams are simultaneously detected with dual InSb detectors located at the focal points. A turret-actuated scrapping mirror allows deflection of the reflected beam upwards, which is then re-directed by a flat mirror through a 25 mm Ge etalon onto the sample beam detector for tuning rate (relative wavelength) determination.

The QCL light pulses are detected with LN_2-cooled photovoltaic (PV) InSb detectors (D* ≈ 8×10^{10} cm·$Hz^{1/2}$/W) operated at relatively high reverse bias voltages for improved linearity. The

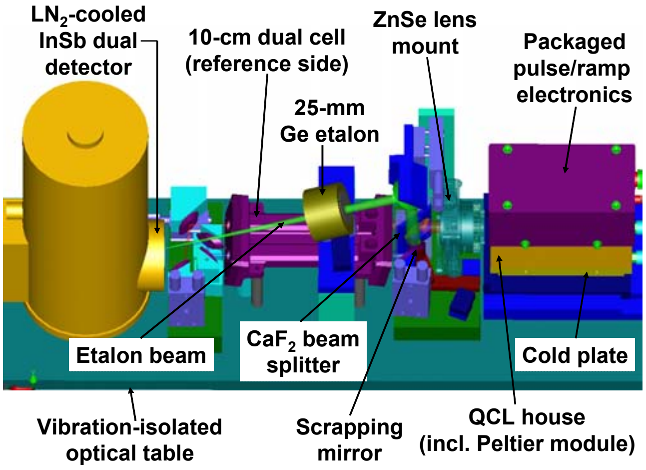

Figure 3: **3-D CAD rendering of the CO_2 QCL spectrometer showing components along with sample, reference and etalon beams as calculated with ray-tracing software.**

detected pulses are time averaged with a detector rise-time matched gate (50 ns) and digitized using 5-Mz, 12-bit PXI ADC/DAC boards. The boards also generate QCL trigger (1 MHz), gate and ramp signals (9 kHz). Details on the pulse electronics are given elsewhere [Jiménez, 2005].

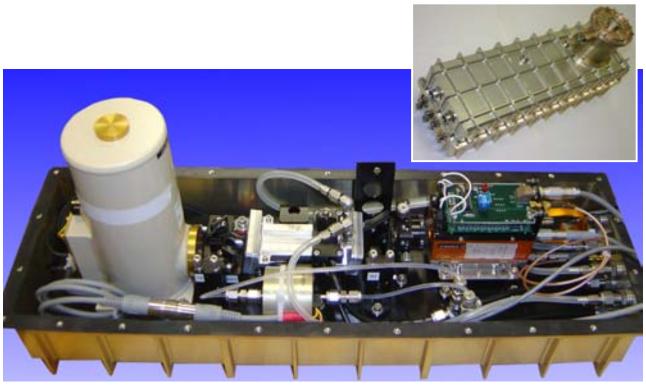

Figure 4: CO_2 QCL spectrometer. The inset shows the pressure vessel in which the optical table is housed. Dimensions: L = 61 cm, W = 20 cm, H = 18 cm + 10 cm dewar hat

The optical and optoelectronic components of the spectrometer (along with absolute and differential pressure transducers and various thermistors) are mounted and stabilized along the detection axis on a vibrationally isolated optical table housed in a hermetically sealed, temperature-controlled aluminium pressure vessel (see Figure 4). Heat generated by the QCL peltier module is dumped into a Peltier-based close-circuit chiller that keeps the coolant temperature controlled to better than ±0.1 K and can operate with dielectric coolants (e.g. Galden® or Flourinert®). Heat generated by other components in the enclosure is negligible. Boiled LN_2 is vented outside the pressure vessel using 2 passive control valves in series. This allows thermostating the InSb detectors by keeping the LN_2 pressure constant at 1055±2 hPa, irrespective of the ambient pressure. Thermal control of enclosure and flowing gases is also better than ±0.1 K. A precision of ±80 mK is achievable in-flight by thermally conditioning the sample gas flow upstream of the absorption cell, and by carefully regulating the absorption cell thermal environment.

Gas entering the sample inlet passes subsequently through a particle filter, a Nafion dryer and a dry ice trap, which reduces [H_2O] to less than 300 ppm, sufficient to limit H_2O-related density effects to less than 0.01%. This along with active temperature, pressure and flow control with thermally stabilized valves and restrictors provides internal density stabilization to 0.015% [Daube, 2002].

Flow rates through sample and reference cells are set at ~100 sccm (~1 s response time) and ~30 sccm, respectively. The sample cell pressure is controlled at ~70±0.1 hPa. We also actively regulate the flow rate through the reference cell to insure a pressure difference between the two cells of less than ±0.01%. A zero or background spectrum is recorded after filling both cells with reference gas. The baselines of background-subtracted differential spectra are well defined by a low order (≤ 2) polynomial, further reducing the uncertainty of the spectral fit. The reference spectrum is also independently fitted to determine the transition peak position and for line locking purposes (computer-commanded adjustment of the central wavelength via QCL temperature). The line position determined from the reference spectra allows fitting background-subtracted differential spectra of “negative” ($\Delta[CO_2] < 0$) or zero absorbance. The pressure vessel is purged with CO_2-free dry air or N_2 previous deployment.

The CO_2 QCL instrument also includes an external pressure and flow control module, a calibration gas deck, and a 4-head diaphragm pump. The computer and other components are shared with a dual QCL spectrometer (CO, CH_4, N_2O) [Jiménez, 2005]. The instrument package consumes ~500 W continuous (1.2 kW max) and weights 100 kg. The modules can be re-distributed to accommodate to various platforms.

The operation of the spectrometers is fully automated and computer-controlled through *TDLWintel* [Nelson, 2006] run on a PXI computer. *TDL Wintel* retrieves, analyzes, and stores the spectra along with housekeeping data. Mixing ratios (and QCL linewidths) are real-time retrieved from the spectra using a Levenberg-Marquardt based algorithm. The data analysis procedure includes pulse normalization, and simultaneous fitting of a low-order polynomial to the spectral baseline and of Gaussian-convolved Voigt [Humlícek, 1982] profiles to the observed transitions.

3.4.4 *What Controls the Precision?*

The short-, mid- and long-term precisions of the CO_2 QCL spectrometer are basically determined by the QCL power and linewidth, the detector (dark) noise, the presence of optical interference fringes, and the stability of the state variables (pressure, differential pressure and temperature). We investigated the precision of the spectrometer as a function of the integration time and the CO_2 mixing ratio difference using the Allan variance concept [Werle, 1993]. We found that dark noise and baseline stability (affected by interference fringes) have comparable contributions (~20 ppb·$Hz^{-1/2}$) to the 1 s precision (see Figure 5). These two components add in quadrature to a lowest achievable precision of ~30 ppb· (1-s, 1-sigma precision). The actual precision at zero mixing ratio difference ($\Delta[CO_2] = 0$) is higher (~45 ppb) as this measurement is affected by the state variables, particularly differential pressure. A nearly proportional increase in noise is observed as sample mixing ratios depart from the reference mixing ratio (see Figure 6). The proportional noise is intrinsic to the absorption spectroscopy technique. Measurements with cells of different length showed, as expected, that the proportional noise rate follows the (apparent) optical thickness. The 10-cm cell (combined with a better detector) provides nevertheless a factor 2 better precision at low mixing ratio differences compared to the 4.7-cm cell. The penalty for the larger proportional noise with the 10-cm cell (0.37 ppb/ppm) is only important for extremely large mixing ratio differences (> 450 ppm).

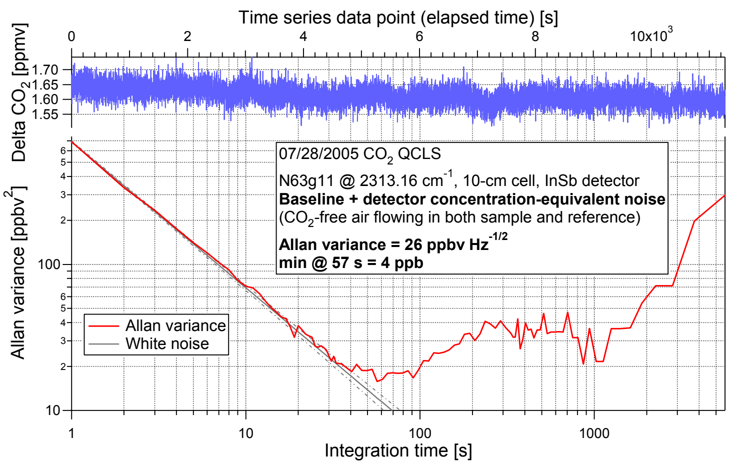

Figure 5: CO$_2$ spectral baseline stability (precision) as a function of integration time (Allan variance). The noise is fully Gaussian within time periods of ~40 s or less. The expected difference between averages of zero-measurement defined data sets is ~6 ppb (1-sigma) or better at zeroing frequencies of 4-6 h^{-1}.

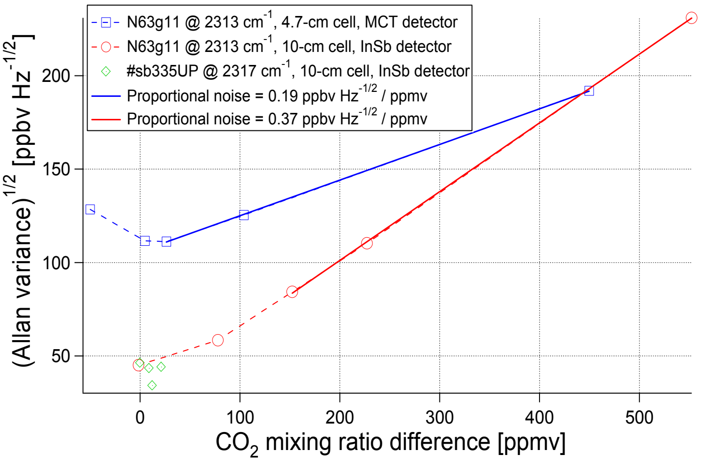

Figure 6: 1-s precision of CO$_2$ measurements as a function of the CO$_2$ mixing ratio difference (reference subtracted [CO$_2$]). There is a minor penalty on precision for infrequently encountered, elevated CO$_2$ concentrations. The precision achieved is reproducible with recently procured QC-lasers that reach the target transition at 2319 cm^{-1} (e.g. #sb335UP).

The demonstrated precision of the CO_2 QCL spectrometer is ~50 ppb (1s, 1 sigma) for mixing ratio differences within ±50 ppm. Mixing ratios differences above this range are only rarely encountered in the free troposphere / stratosphere (provided the reference mixing ratio is close to the tropospheric background ~380 ppm).

3.4.5 Conclusions and Perspectives

The new airborne CO_2 QCL spectrometer provides improved linearity and comparable short-term precision to mature NDIR instruments. The new instrument currently achieves a short-term precision of better than ~50 ppb (1s, 1-sigma) for the mixing ratio differences (sample – reference) typically encountered in airborne missions ($|\Delta[CO_2]| < 50$ ppm). Further precision improvement is expected through fine tuning at the optimum wavelength (2319 cm^{-1}). An accuracy of ± 0.1 ppm or better is ensured through periodic calibration with high, low and long-term surveillance standards traceable to NOAA/ESRL.

The new spectrometer is also suitable for eddy covariance measurements. Measurements of the CO_2 isotopic composition have been demonstrated with the same or similar QC lasers operated in similar spectrometers [McManus, 2005; Saleska, 2005; Weidmann, 2005].

Our spectrometer could be easily modified to operate with TEC CW-QC lasers when these become more available, and with TEC PV detectors provided their saturation behaviour is significantly improved in the future. Nelson *et al* [2006] have recently demonstrated long-term cryogen-free operation with a similar QCL spectrometer.

3.4.6 Acknowledgements

We gratefully acknowledge the contribution of Jeff Mulholland, Daniel Glenn and Patrick Kirwin (Aerodyne Research, Inc.) to the engineering, design, and construction of the spectrometer here presented. We also thank Alpes Lasers for providing the lasers and high quality components used in our systems, and their technical advice and assistance. Funding for instrument development has been provided by the DOE STTR and SBIR programmes, and the NSF MRI and HIAS programmes.

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3.5 On Thermal Fractionation Effects at Air Intakes

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3.5.1 Introduction

Atmospheric oxygen is a useful tracer, which helps to constrain carbon fluxes, but the required relative precision for such measurements is in a range where experimental artifacts like fractionation effects and gas handling procedures become absolutely crucial. Fractionation of O_2/N_2 has been observed to occur at tees as well as at the intake and has been attributed to molecular thermal diffusion (Manning, 2001). Thermal diffusion results from temperature gradients. Heavier molecules generally accumulate in the colder region hence leading to concentration changes.

Understanding and quantification of such artifacts is not only highly relevant to O_2/N_2 measurements, but also to Ar/N_2 and to a minor degree to very precise CO_2 measurements. In particular, the Ar/N_2 ratio which can be measured simultaneously with O_2/N_2 by mass spectrometry is a useful tracer to reveal fractionation effects. Only the temperature dependence of the gas solubility in seawater leads to seasonal variations in air-sea fluxes and small changes in atmospheric Ar/N_2 ratio (Keeling et al., 2004). On diurnal timescales, however, the atmospheric Ar/N_2 ratio is expected to be constant, because no biogeochemical processes influence these inert gases. However, continuous Ar/N_2 measurements of air from the roof of our institute (Sturm et al., 2005) showed a large diurnal variability which was attributed to temperature variations at the air intake that lead to thermal fractionation of the sample air.

3.5.2 Results and Discussions

An example of diurnal variations of Ar/N_2 and outdoor temperature are shown in Figure 1. The air intake was a Dekabon tube with a 4mm inner diameter (ID) orifice and the flow rate was about 250mL/min. The outdoor temperature was measured by a HOBO H8 data logger (Onset Computer Corporation, MA, USA) placed at the bottom of the intake pole. The higher the air temperature is, the lower the Ar/N_2 gets.

Variations of the laboratory temperature can also potentially influence the Ar/N_2 measurements. Especially in summer there is a diurnal cycle of the laboratory temperature with amplitudes of 2 to 3°C. However, the most striking feature of the diurnal temperature variations in our laboratory is a rapid drop of about 3°C at midnight caused by the air-conditioning. Because in these experiments no change in Ar/N_2 can be observed at midnight, the variations in Ar/N_2 are indeed mainly caused by fractionation at the air intake. This supposition was further confirmed by actively heating the intake tube, which resulted in large Ar/N_2 deviations.

To assess the causes of the observed Ar/N_2 variations and to better quantify this effect, we conducted tests with different intake tubes and sampling flows. In addition to the Dekabon tube with flow rates of 250mL/min and 35mL/min, a stainless steel tube with 0.8mm ID and a flow rate of 155mL/min was also used. The correlation of Ar/N_2 and outdoor temperature for different types of air intakes is shown in Figure 2. Remarkably, the temperature records lagged the Ar/N_2 variations by 90 to 150min. This is probably due to a slow response of the temperature logger used for these tests and the fact that the temperature sensor was not exposed to sunlight in contrast to the air intake. This time shift was applied in Figure 2 to obtain the best correlation. The temperature sensitivities obtained by geometric mean regression are -17.5±0.6 per meg/°C ($R^2=0.70$), -7.2±0.2 per meg/°C ($R^2=0.71$) and -3.6±0.2 per meg/°C ($R^2=0.51$) for the “4mm,35mL/min”, “4mm,250mL/min” and “0.8mm,155mL/min” experiments, respectively. As shown in Figure 3, the temperature sensitivities of Ar/N_2 mainly depend on the gas velocity at the air intake.

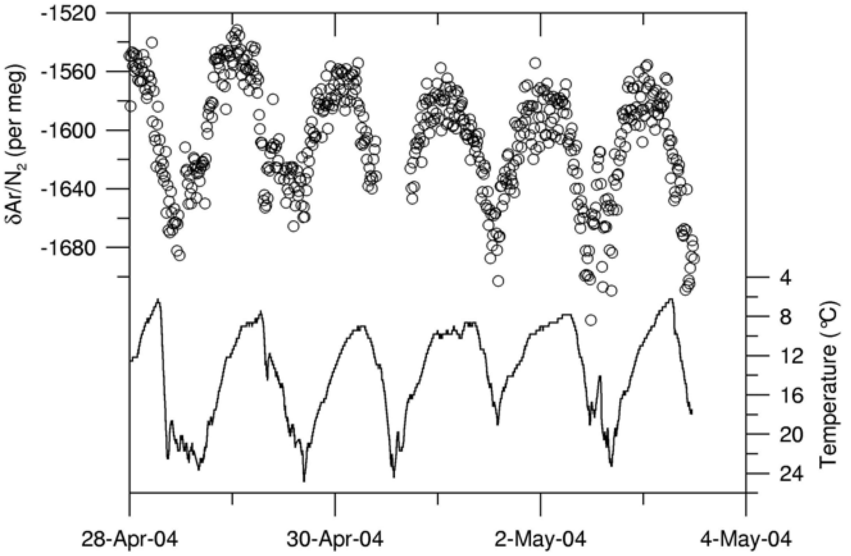

Figure 1: **Diurnal variations of Ar/N_2 (top) and outdoor temperature (bottom). Note the inverted axis of the temperature.**

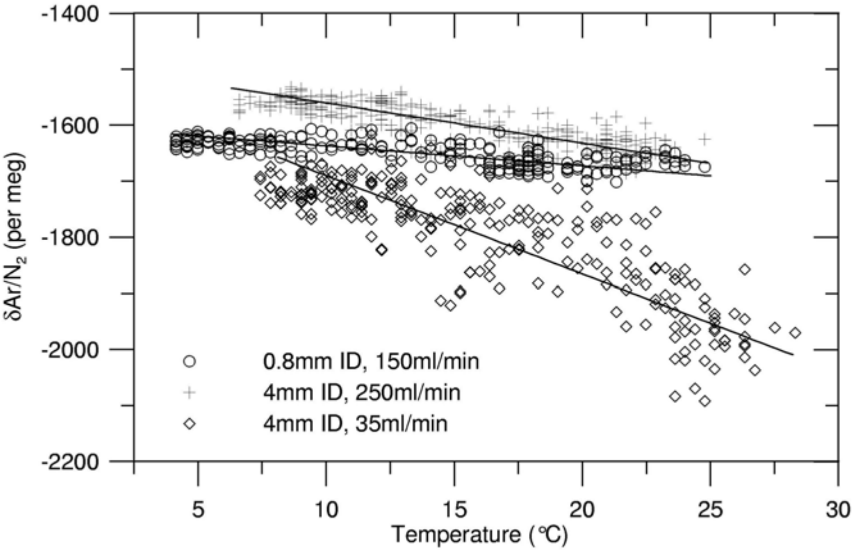

Figure 2: **Lagged correlation of Ar/N_2 and outdoor temperature for different types of air intake.**

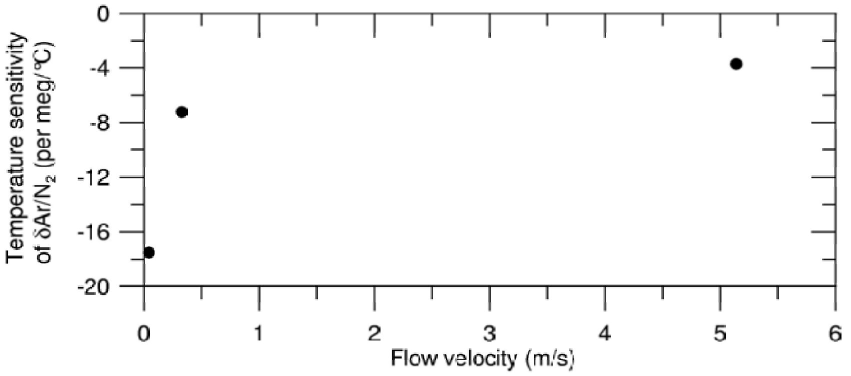

Figure 3: **Temperature sensitivity of Ar/N_2 depending on the gas velocity at the air intake for the three experiments of Figure 2.**

An explanation is that during the day especially when the sun heats the black coating of the Dekabon tube, a small temperature gradient builds up between the intake tube and the surrounding air. This leads to thermal diffusion with preferential accumulation of the lighter molecules in regions with higher temperatures. A thermal diffusion factor for Ar in N_2 of 0.071 (Grew and Ibbs, 1952) would lead to a steady state fractionation of 240per meg/°C. However, a steady state is not achieved at the intake because of the continuous flow of gas. However, the lower the flow velocity the more the air can approach a steady state.

The slope of the correlation plot of Ar/N_2 versus O_2/N_2 for the “4mm,35mL/min” and the intake heating experiments gives 3.8±0.1 (Figure 4a) and is in good accordance with what is expected from thermal fractionation (Table 1). The isotopic ratios $\delta^{29}N_2$, $\delta^{34}O_2$ and $\delta^{36}Ar$ show also small variations that are correlated with the temperature, providing compelling evidence of diffusive fractionation. However, the signal-to-noise ratio relative to measurement precision is much higher for Ar/N_2 than for $\delta^{29}N_2$, $\delta^{34}O_2$ or $\delta^{36}Ar$, because Ar/N_2 is more sensitive to mass-dependent fractionation processes owing to the comparatively large mass difference between Ar and N_2. Figure 4b, c and d show the correlation plots of Ar/N_2 versus $\delta^{29}N_2$, $\delta^{34}O_2$ and $\delta^{36}Ar$ for the “4mm,35mL/min” experiment. The mass spectrometric uncertainty is indicated by error bars in the lower right corner of each plot. Accordingly, the regression lines (black lines) were calculated in Figure 4a, b and c using a measurement error model which accounts for the relative magnitude of the errors in both variables. There is no correlation between Ar/N_2 and $\delta^{36}Ar$ (Figure 4d). The thermal diffusion factors of $^{29}N_2$-$^{28}N_2$, $^{34}O_2$-$^{32}O_2$ and ^{36}Ar-^{40}Ar at 20°C are about 0.0045, 0.0099 and −0.0137, respectively (Lang, 1999). The expected correlation slopes for thermal diffusion obtained from these diffusion factors are shown as grey lines in Figure 4 and summarized in Table 1.

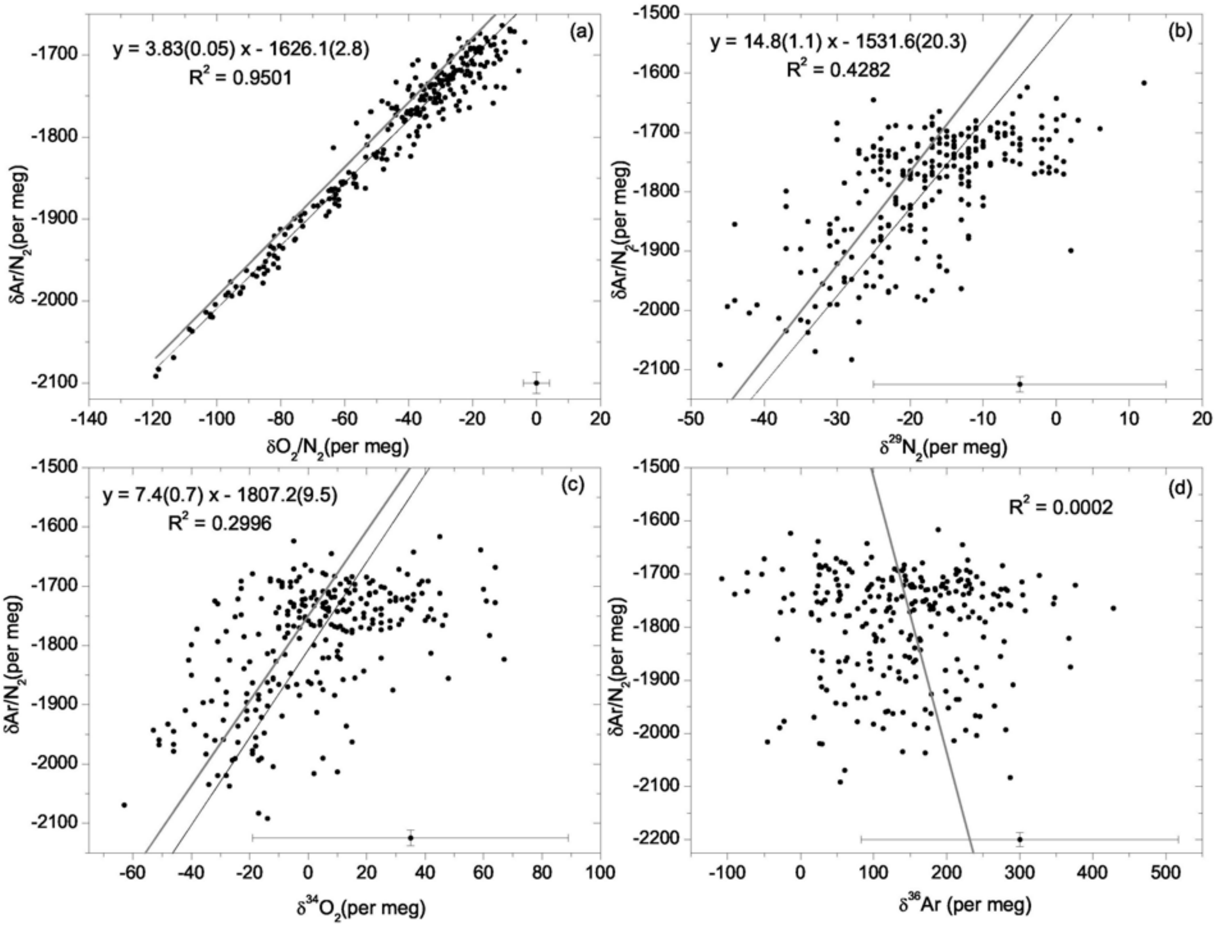

Figure 4: **Correlation plots of Ar/N_2 versus O_2/N_2, $\delta^{29}N_2$, $\delta^{34}O_2$ and $\delta^{36}Ar$. Black lines are the measured regression slopes using the associated errors as shown in the lower part of each graph. Grey lines represent the expected correlation slopes obtained from thermal diffusion factors.**

Table 1: **Thermal diffusion fractionation ratios.**

	measured	literature	
Ar/N_2 - O_2/N_2	3.8 ± 0.1	3.77 ± 0.04 3.9	(Keeling et al., 2004) (Grew and Ibbs, 1952)
Ar/N_2 - $\delta^{29}N_2$	14.8 ± 1.1	15.8	(Lang, 1999)
Ar/N_2 - $\delta^{34}O_2$	7.4 ± 0.7	7.2	(Lang, 1999)

Additional tests with sample air from a high pressure cylinder showed that there is also a measurable influence of the laboratory temperature on our Ar/N_2 measurements. A cylinder was placed outside the laboratory where only small and not abrupt temperature variations occur, to exclude any fractionation related to the cylinder or the pressure regulator. Then, the measured Ar/N_2 showed a positive correlation with the laboratory temperature (in contrast to the negative temperature sensitivity for fractionation at the intake). Different sources of thermal fractionation inside the laboratory may lead to these effects: a) The cold trap which is partly immersed in silicon oil at -70°C. Because of the relatively large volume (~250mL) and the large temperature gradient (~90°C) thermal diffusion is likely to occur inside this cold trap. Changing temperature gradients due to varying room temperatures could therefore lead to thermal effects. b) Temperature dependent fractionation at tees (Manning, 2001), and c) Fluctuations of the working gas due to thermally induced effects at the high-pressure gas cylinders.

Experiments showed that the fractionation at the intake can be reduced if instead of Dekabon, other types of tubing are used. Intake tubes both made of transparent plastic and stainless steel significantly reduced this effect, presumably because of a smaller influence of solar heating. However, thermal fractionation could also be observed on days with overcast sky. Shading of the intake from sunlight can therefore only reduce but not eliminate this effect. A more effective protection of the intake orifice from solar radiation is therefore needed to minimize fractionation effects. High flow velocities at the intake either by large sampling flows or by intake tubes with small orifices may also be helpful for reducing thermal diffusion at the intake.

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4. REGIONAL OBSERVATIONS

4.1 First Continuous CO_2 and O_2 Measurements on Jungfraujoch, Switzerland

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Abstract

Continuous analyses of CO_2 and O_2 have been made at the high alpine research station Jungfraujoch. The measurement system used is a custom-made instrument based on a commercially available infrared CO_2 absorption laser and a combined fuel cell and paramagnetic technology for oxygen. Measurements have revealed that the precision for the paramagnetic cell matches our requirements of 5 per meg at the 10 second time level, whereas the fuel cell precision lacks this requirement even when averaging over time periods of several minutes. However, it is been observed that this inadequate precision is due to small temperature fluctuations within the fuel cell despite the fact that air temperature is controlled to better than 0.1 K and with a stability of the fuel cell block temperature of better than 0.02 K. From our measurements we derive a temperature sensitivity of about 40μV/°C. This can be transferred to an oxygen sensitivity of 3.6 per mil/K or 4 per meg/mK. Hence a temperature control to the mK level is required or an experimental procedure to compensate this temperature influence has to be applied.

The results of the continuous measurements support the seasonal amplitude derived from flask determinations in both CO_2 and O_2 but document additional short term variations that is twice to three times larger. The calculated slope (O_2/CO_2) of the continuous O_2 and CO_2 data vary from 1 mol/mol up to values significantly larger than 2 mol/mol. The values around 1 are predominantly found during summer months in agreement with expectations from interactions with the biosphere. The higher values occur sporadic but can remain for a couple of days up to one week. Back trajectory calculations indicate influences from ocean exchanges. However, this interpretation is preliminary due to only a one year observation.

4.1.1 Introduction

The high alpine research station on Jungfraujoch celebrates its 75th anniversary in 2006. This station is a GAW and is well known for its long term measurements for carbon-14 (^{14}C), cosmic rays and it is a central station for ozone and aerosols. Since 2000 flasks samples have been taken for air composition analyses, mainly CO_2 and O_2 at the Physics institute of Bern, Switzerland. Figure 1 summarizes these measurements.

Since the calculated seasonal slope of less than -2 mol O_2/mol CO_2 is unexpected a more detailed view of the evolution of oxygen and carbon dioxide is necessary. Therefore, we built our continuous system for the Research Station at Jungfraujoch. The layout has been given in the report for the 12th CO_2 Experts meeting [*Leuenberger*, 2005]. Several views of the instrument are given in Figure 2. The CO_2 analyser is commercially available Sick Maihak S700 analyser that has been shown to be very temperature stable. At JFJ, we use secondary standards which are calibrated in our laboratory at BERN to standards purchased from the NOAA/ESRL Carbon Cycle Greenhouse Gases Group (CCGG), who is presently responsible for maintaining the WMO mole fraction scales for CO_2, CH_4, and CO.

For the oxygen measurements we have installed one paramagnetic cell manufactured by MBE in Wetzikon, Switzerland and four fuel cells from Maxtec MAX-250, USA. Great emphasis has been given to control temperature, pressure and gas flow to an extremely high level in order to minimize influences of those parameters. Pressure is maintained by an absolute pressure transducer and a 1 mbar differential pressure gauge combined to a control valve made by MKS, Germany. The gas paths are controlled at the beginning by valco valves but due to several failures replace by a setup of Clippard valves. The resolution of data collection is 1 second, mainly to understand the instrument performance rather than to gain information about the short term variations in the atmosphere. This high resolution leads to a large accumulation of data but for certain questions it is necessary as will be pointed out below.

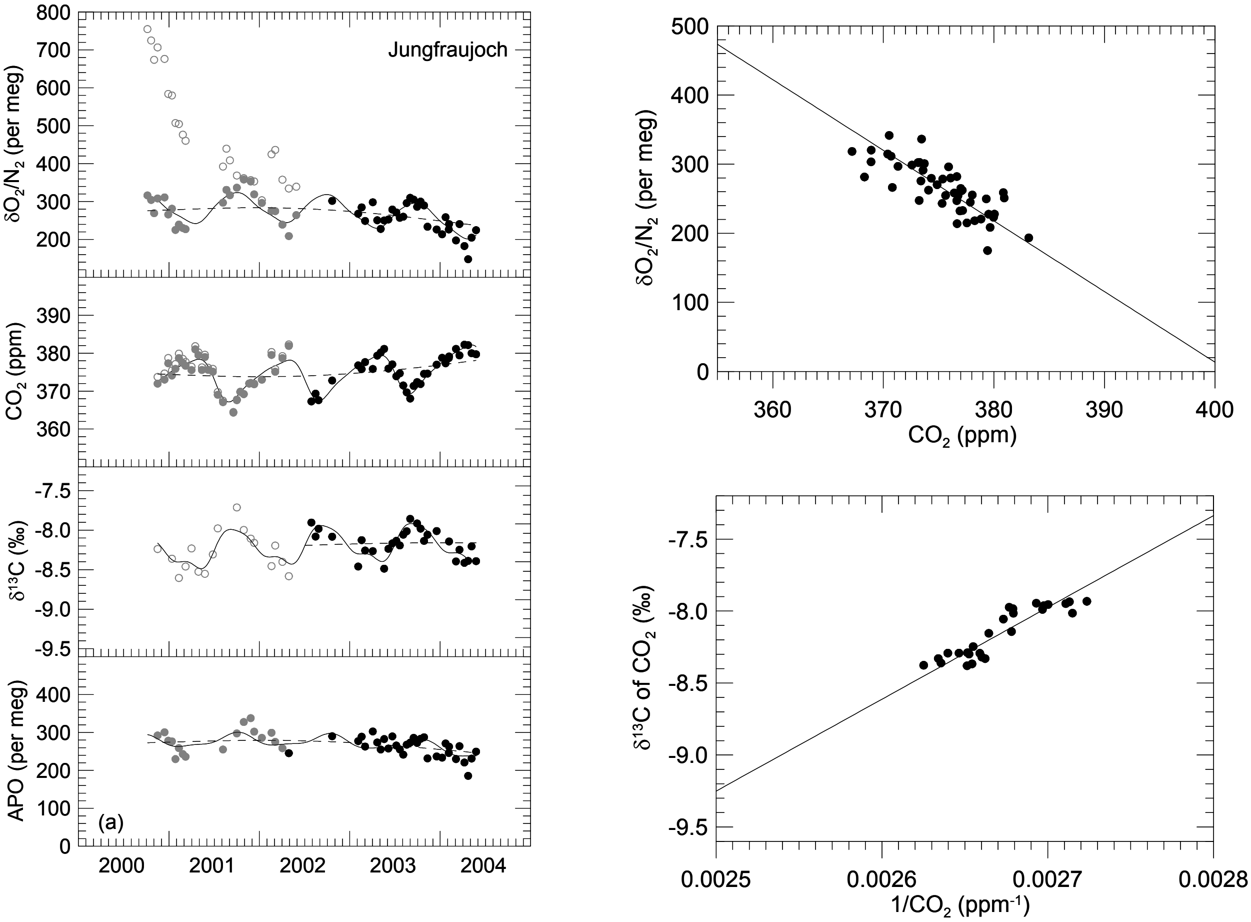

Figure 1: (left) Flask measurements at the high alpine research station Jungfraujoch after Sturm et al.[2005]. Open circles are uncorrected values, grey dots are permeation corrected values after Sturm et al. [2004]. Black dots are measurements after sampling procedure improvements significantly reducing the permeation influence. (right, top) Correlation plot for O_2/N_2 versus CO_2. The calculated slope is less than -2 molO_2/mol CO_2. (right, bottom) Correlation plot for $\delta^{13}C$ versus the inverse CO_2 concentration (Keeling Plot). The calculated end member is between -24 and -29.5 permil.

4.1.2 Results

The instrument was installed in December 2004. During 2005 we tried to keep the instrument running as much as possible. But due to several problems associated with valve malfunction as well as badly tuned control parameters we had to deal with many interruptions. The interruptions were less severe for CO_2 than for O_2 since the control requirements are less stringent for the commercially available CO_2 analyser. However, significantly more than 50% of the 2005 data are covered with measurements. The variations of both parameters are given in Figure 3. The measurement precision is better than 0.1 ppm for CO_2 and better than 10 per meg for O_2 based on the paramagnetic cell. The CO_2 concentration ranges between 365 and 405 ppm, whereas oxygen range between 0 and 270 per meg on the BERN-oxygen scale, which is presently compared to other laboratory oxygen scales. The variability is of course much less compared to variations seen at Bern city which is between 360 to more than 500 ppm [*Sturm et al.*, 2006]. The squares represent the flask samples taken within the CarboEurope IP project. The flask – *in situ* agreement is good even for high values (outliers) since the online measurements showed significant short term (hourly to daily) variations. One conclusion from this comparison that can be drawn is that the flask sampling should be done at early morning hours (at least at Jungfraujoch) when hardly any influence from upslope air flow is observed. Otherwise, the extracted seasonal signals from weekly or bi-weekly measurements can be significantly disturbed by variations throughout the day.

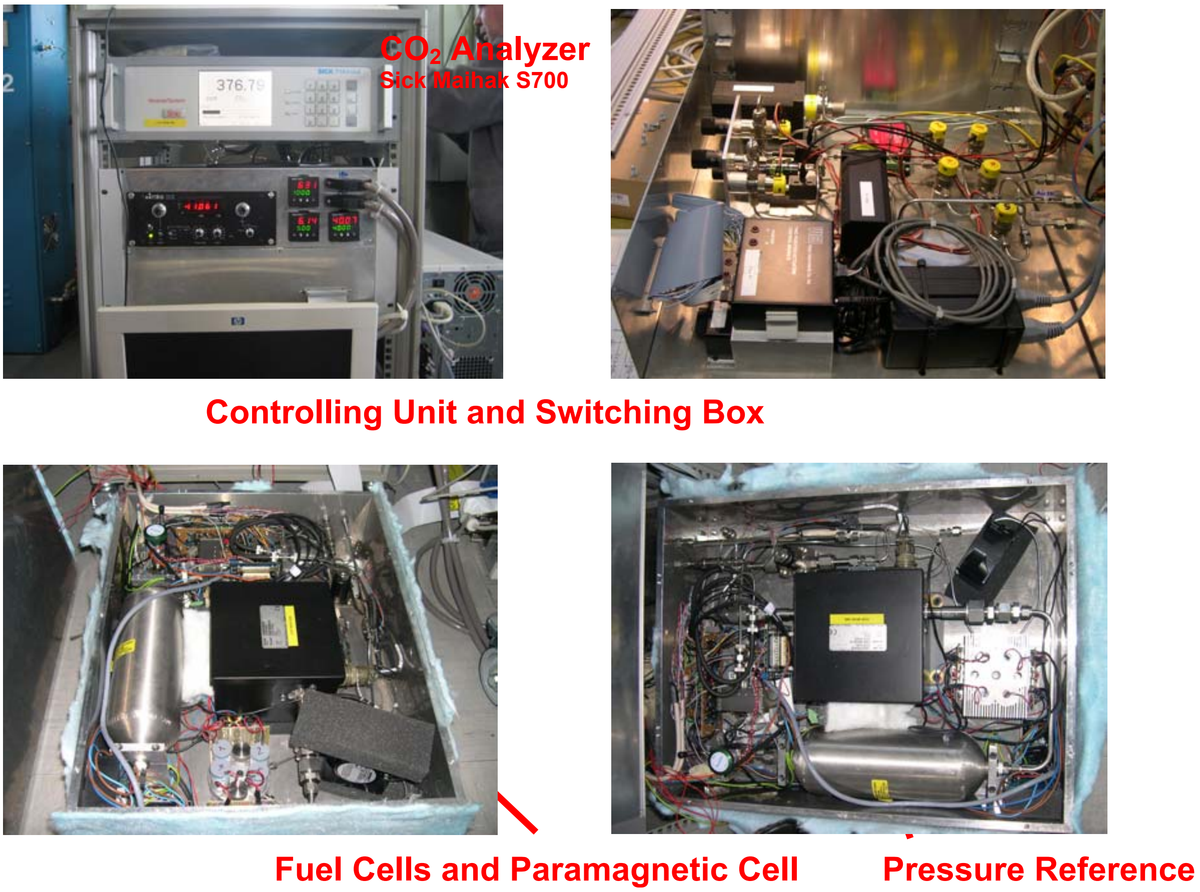

Figure 2: Several pictures of the online instrument for CO$_2$ and O$_2$ on Jungfraujoch.

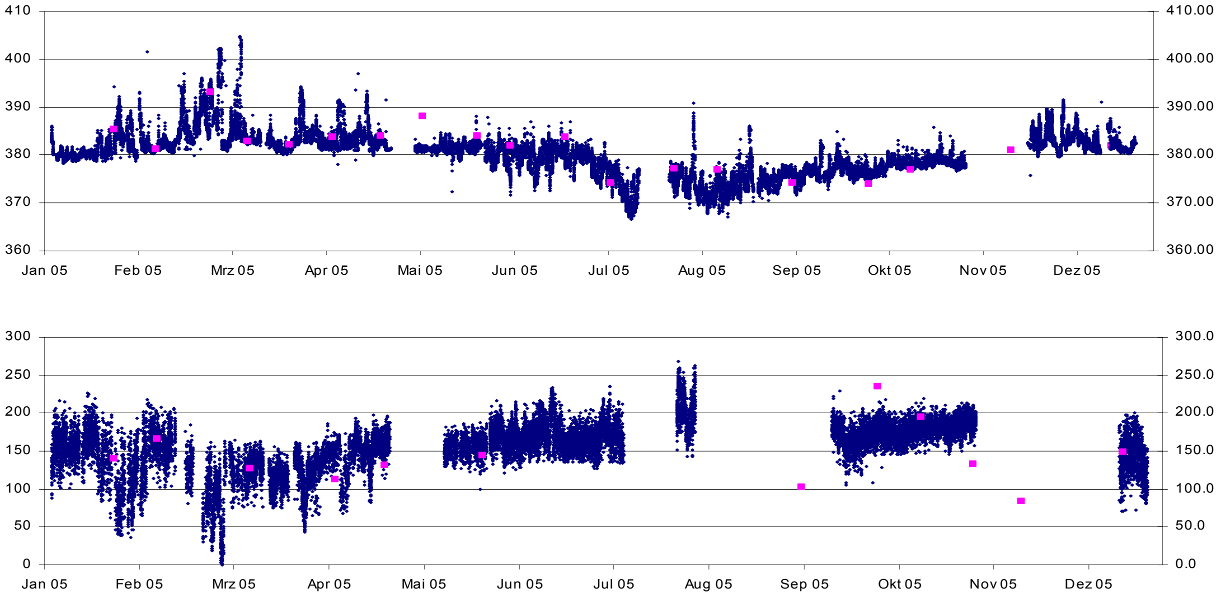

Figure 3: Carbon dioxide and oxygen concentration at the High Alpine Research station Jungfraujoch, Switzerland for the year 2005. Upper panel: CO$_2$ concentration in ppm, lower panel O$_2$ concentration in per meg. Blue dots represent in situ measurements and pink squares, flask measurements.

When we zoom in, clear correlations between CO_2 and O_2 measurements are observed despite the rather small ranges. As examples, we summarize three different periods in February and June 2005. The first two panels of Figure 4 are short term variations (minutes to hours), whereas the bottom panel depicts half daily values of the whole month of June 2005. The oxidation ratios are highly variable, for these three time-frames between -1.31 to -2.47 mole oxygen per mole carbon dioxide. These slopes have been calculated using the quadratic mean regression rather than the simple linear regression technique which will lead to smaller slopes (which are proportional the correlation coefficient). It will be important to check the online data for the variability of these slopes. Preliminary results of back trajectory calculations seem to support a strong influence of the ocean to explain the very low oxidation ratios of below -2 mol oxygen per mol carbon dioxide.

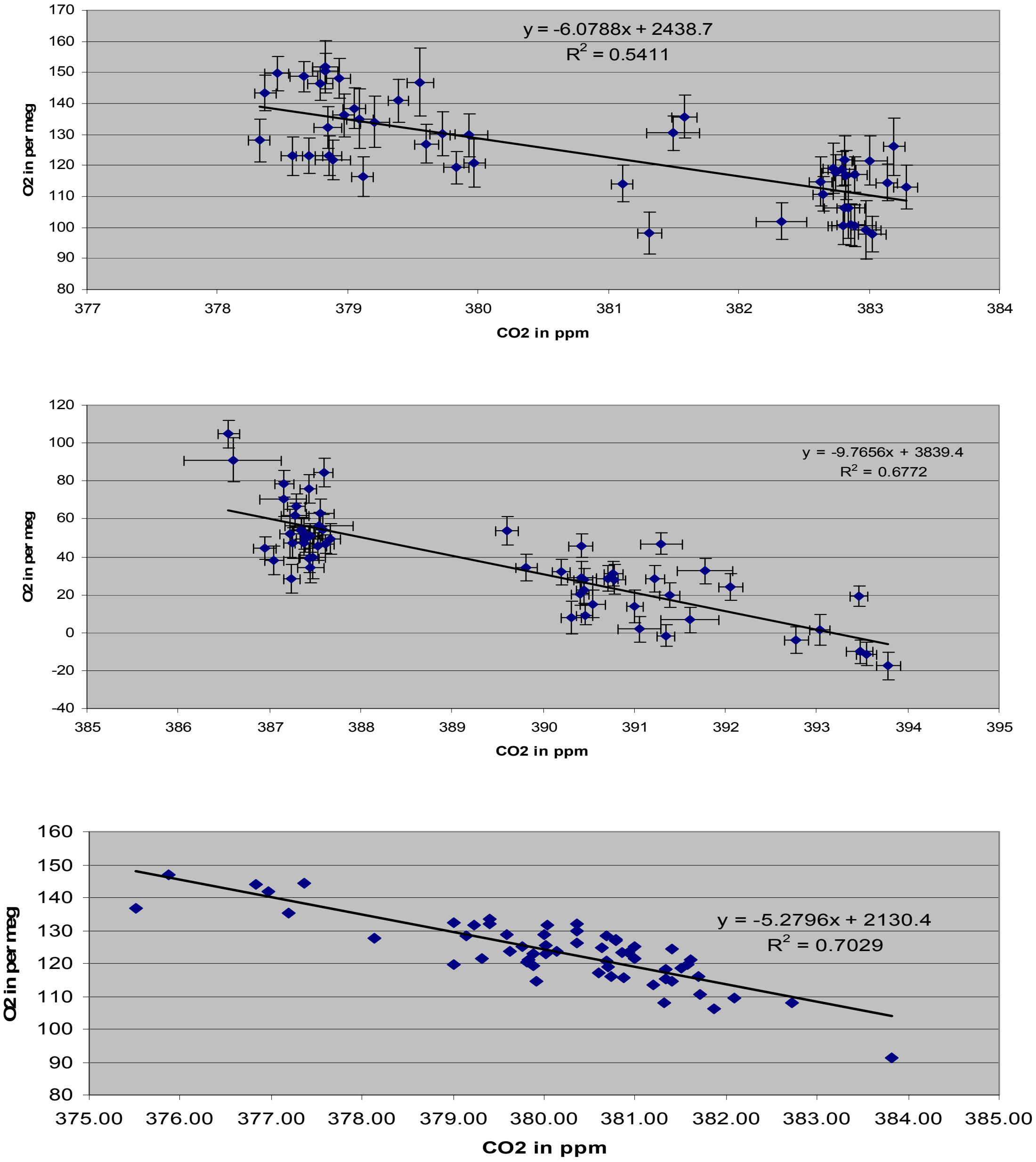

Figure 4: **Oxygen to carbon dioxide relationship for three different periods. (top) 14th of June 2005 for 4 minutes averages, (middle) 25th of February 2005 for 3.5 minutes averages, (bottom) June 2005 for half daily values. The corresponding mol oxygen to mol carbon dioxide relation are (top) -1.72 mol/mol, (middle) -2.47 mol/mol, (bottom) -1.31 mol/mol.**

Up to now, we still do not understand the much lower precision of the fuel cells in detail. But what we clearly detected is a very strong dependence of the fuel cell signals to temperature variations. Despite the temperature control to better than 0.1 K for the air temperature within the measuring box, a clear dependence on temperature has been found. We derive a temperature sensitivity of about 40μV/K that can be transferred to an oxygen sensitivity of 3.6 permil/K or 4 permeg/mK. This requires a temperature control to the mK level which is experimentally very difficult to reach. Therefore, we think that another approach has to be taken, maybe in a similar way as outlined by the commercially available Oxzilla instrument. This instrument uses two fuel cells to cancel out short term variations due to any kind of influences but we believe that they are mainly variations due to small temperature fluctuations.

This temperature dependence has been analysed in detail for our system and we found that there are signal transmissions in different frequency ranges. One frequency is given by the temperature controller itself that pulses the electrical area heating elements roughly four times per second. The other frequency is given by the response time of the whole temperature controlled box to an applied temperature change. The latter is much longer and as based on a comparison between the paramagnetic cell and the fuel cell corresponds to about one to two hours. Figure 6 is a zoomed version of Figure 5 for the period of the 5th to the 9th of April in 2006. This similarity between the two principles to measure oxygen is encouraging since now, we will be able to modify and adapt our methods to minimize this observed strong temperature influence or correct for it. The four fuel cells behave very similar as can be seen in Figure 7 and 8.

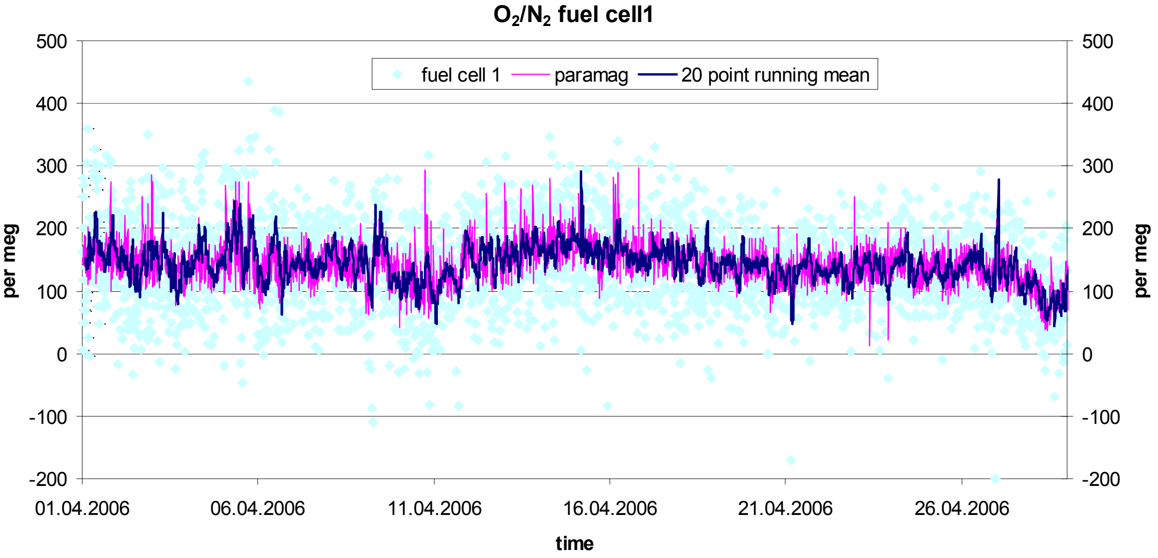

Figure 5: **Comparison between the paramagnetic cell given in pink colour and the fuel cell 1 signal in light blue and a 20 point running mean of the fuel cell data in dark blue.**

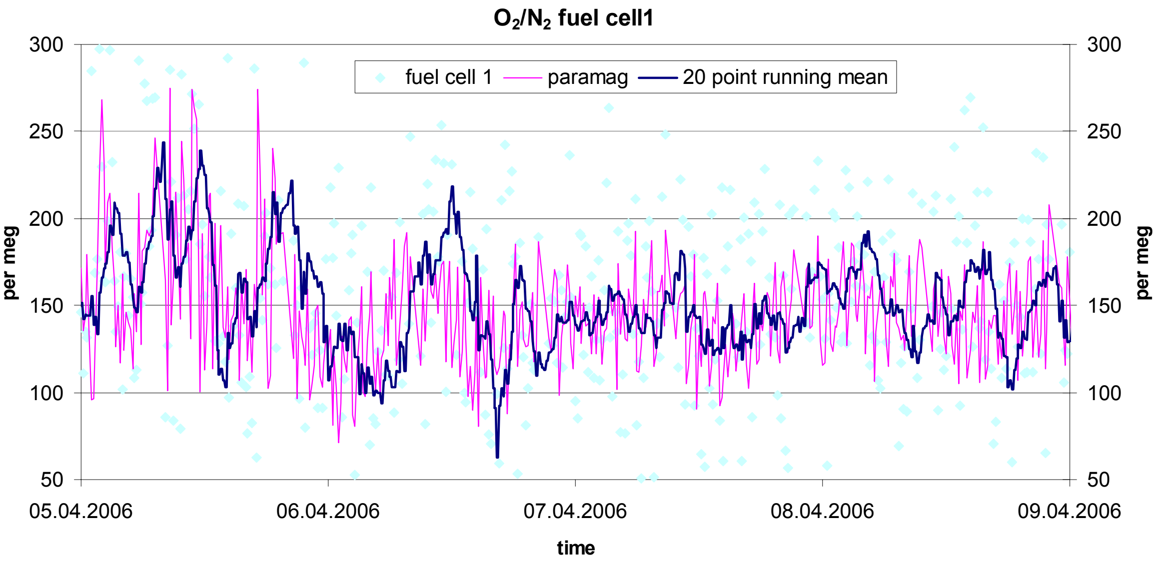

Figure 6: Zoom in of figure 5 for the period of 5th to 9th April in 2006. An obvious relationship between the averaged fuel cell and the paramagnetic cell signals is present.

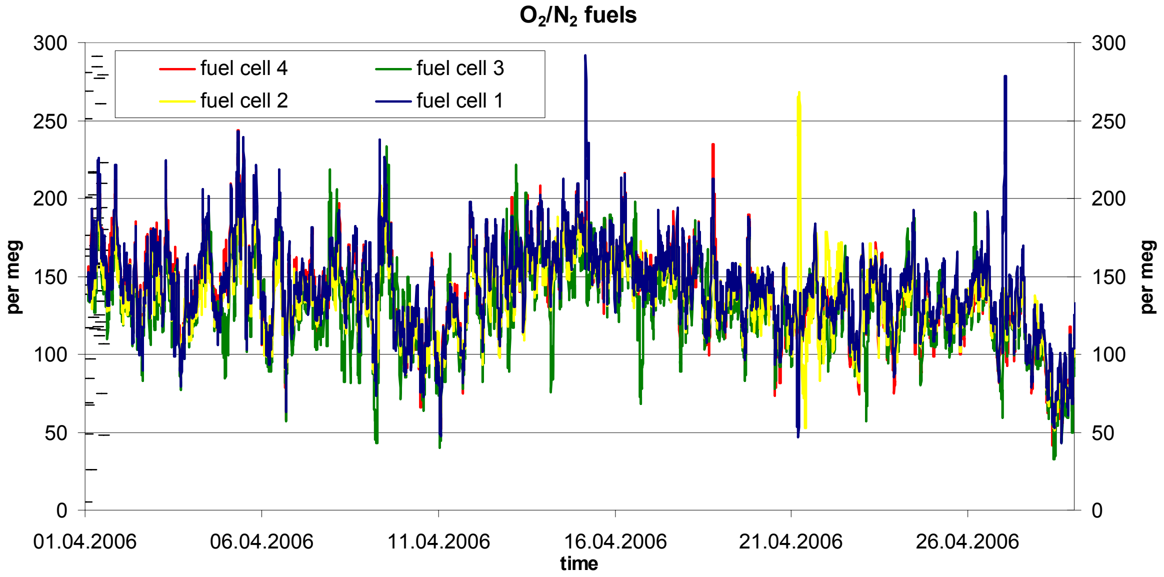

Figure 7: Comparison of the four fuel cells after applying a 20 point running mean. The long term pattern is consistent between all cells.

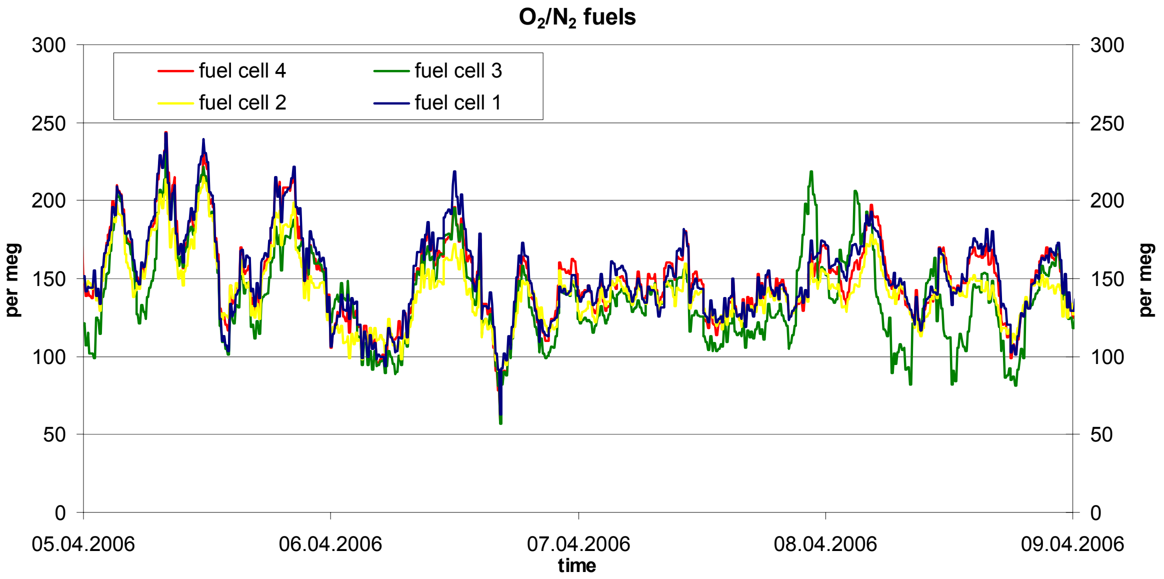

Figure 8: **Zoom-in of figure 7 for the period 5th to 9th April 2006. It documents that also the hourly variations are quite synchronous. Fuel cell 3 deviates during certain time frames significantly.**

4.1.3 Conclusions

First continuous measurements have been obtained at the High Alpine Research Station Jungfraujoch. Data coverage of significantly more than 50% for the first year is very promising. The O_2:CO_2 relationship varies considerably at Jungfraujoch documenting that in addition to the influence of continental air, long term transport signals from the ocean may also be recorded based on the very low oxidation ratios.

A comparison between the two oxygen measuring techniques has revealed an extremely strong temperature dependence of the fuel cells. Based on these findings either a redesign of the temperature control has to be envisaged to minimize this influence or a procedure to mathematically account for this influence.

Acknowledgements

We would like to thank the MBE AG in Wetzikon, Switzerland for constructing in collaboration with us a prototype of a precise paramagnetic cell. This project was supported by the CARBOEUROPE IP project (GOCE-CT-2003-505572) and the Bundesamt für Bildungswesen (BBW-NR. 03.0350-2).

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4.2 Measurements of Greenhouse Gases Contents in the Air near the Ground and in the Atmospheric Column to Study Their Variability

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4.2.1 Introduction

Control of carbon dioxide (CO_2), methane (CH_4) and carbon monoxide (CO) burdens in the atmosphere will require knowledge of their mixing ratios in air samples taken near the ground. Measuring ground-based air samples is very accurate as it is based on a comparison of CO_2, CH_4 and CO abundance in air samples relative to reference gas mixtures. Its use is most effective in places located far from anthropogenic and natural sources of these gases. However, in continental environments the measurement results obtained with this method may not be representative due to the influence of local ground-based sources and sinks of the gases.

The method of solar radiation absorption spectroscopy used for studies of atmospheric gas composition is also known well. It is based on the determination of CO_2, CH_4 and CO abundances from the spectra of solar radiation passing through the entire thickness of the atmosphere. The measurement results obtained with the use of this method are the column-mean mixing ratios of CO_2, CH_4 and CO. Though the uncertainties in the spectroscopic measurements are higher than in situ measurements, they are not strongly affected by local surface sources and sinks of these gases.

The application of both kinds of measurements on one gas in the air near the ground and in the atmospheric column obtained at an observation site makes it possible to compare the results and investigate the vertical propagation of these gases in the atmosphere from ground-based sources. Therefore, in Obninsk (55.11^0 N, 36.57^0 E, 183 m above the sea level, in the European part of Russia) measurements of CO_2, CH_4 and CO near-surface and column-mean mixing ratios have been started.

4.2.2 Instrumentation Complexes and Measurement Methods

4.2.2.1 Instrumentation and Method to Study Variations of CO_2, CH_4 and CO Concentrations in Air Samples

The instrumentation system designed for measurements of CO_2, CH_4 and CO mixing ratios in air samples includes the Perkin–Elmer 1720 Fourier spectrometer, a multi–pass optical cell and a technological scheme (Baranov et.al., 1999). The Fourier spectrometer has a limited spectral resolution of 0.5 cm^{-1} and an operating range of 400 - 5000 cm^{-1}. The multi–pass optical cell was developed and manufactured at SPA "Typhoon". It provides a 30 m absorbing path length in a 1 m cell and a volume of about 12 L. The gas-handling system is used for filling and evacuating the cell and for temperature and pressure control. The measurements are made according to the method applied to single–beam devices. The transmission spectra of the cell is recorded both after evacuation and backfilling with sample air.. The ratios of the resultant spectra are calculated and result in a normalized spectrum of air transmittance (Figure 1). The time needed for analyzing one sample is about 12 minutes.

Mixing ratios of CO_2, CH_4 and CO are determined by comparison of an experimental spectrum with that calculated with the parameters of spectral lines from the HITRAN–04 database. Random errors resulting from retrieving the mixing ratios of the gases studied according to the experimental spectrum are given in Table 1. The statistical estimate of a random error for typical mixing ratios was obtained by computing the error matrix based on the noise level of recorded spectra. A real random scatter of concentrations obtained from the reproducibility of measurement results appeared to be almost two to three times less than the statistical estimates of a random measurement error. A possible systematic error may result from inaccuracies of spectral line parameters from the HITRAN–04 database. Other sources of systematic errors are negligible.

Table 1: **Random errors of measurement results.**

Gas constituent	CO_2 (ppm)	CH_4 (ppb)	CO (ppb)
Statistical estimate	**±2**	**±300**	**±10**
Reproducibility of results	**±1**	**±10**	**±3**

4.2.2.2 Instrumentation and Method to Study Variations of CO_2, CH_4 and CO Column-mean Mixing Ratios

The instrumentation system (*Kashin et. al., 2001*) for determining CO_2, CH_4 and CO in the atmospheric column consists of a system for following the Sun, a spectrometer and a computer to control the system, to preliminarily process data and to form an archive of experimental spectra. The spectrometer has a spectral resolution of 0.2–0.4 cm^{-1} in the operation range of 2000 – 5000 cm^{-1}.

The method *(Kashin et.al., 2000)* is based on the registration of solar radiation spectra in the range of CO_2, CH_4 and CO absorption bands and the subsequent determination of the transmission function within the operational spectral ranges. The mean mixing ratios of CO_2, CH_4 and CO in the atmospheric column are found from the transmission function, the dependence of which on column abundance is calculated with the use of the spectrum fine structure parameters, monthly mean model vertical profiles of pressure, temperature and humidity along with vertical distributions of CO_2, CH_4 and CO in the atmosphere. The registration of solar radiation spectra is made during the daytime at different solar zenith angles. The mixing ratios of CO_2, CH_4 and CO measured along the inclined path are recalculated relative to their column mixing ratios.

The random instrumentation errors in single column measurements of CO_2, CH_4 and CO are 2 %, 4% and 4%, respectively. The systematic error is determined over the accuracy of spectral lines parameters from the HITRAN–04 database and also by the error in the pressure and humidity vertical distributions used. The error in the vertical distributions is a systematic one for a certain measurement day but becomes a random error for monthly mean CO_2, CH_4 and CO.

4.2.3 Results of Comparison of CO_2, CH_4 and CO Mixing Ratio in Air near the Ground and in the Atmospheric Column

A direct comparison of CO_2, CH_4 and CO contents in the air near the ground and in the atmospheric column is impossible because they represent different parts of the atmospheric column. The first-mentioned group characterizes a mixing ratio in an air sample near the ground, and the second one characterizes the mean atmospheric column mixing ratio. One way to compare these data assumes that CO_2, CH_4 and CO are uniformly mixed in the column. In this case their mixing ratios are constant with height. Under such an assumption it is possible to recalculate a height-averaged mixing ratio. Another method does not assume uniform vertical distribution, but instead uses model vertical distributions of the mixing ratios. Below are shown the data for CO_2, CH_4 and CO obtained from the measurement results for mixing ratios with the results of measurements of the column abundance and model vertical distributions.

Carbon dioxide. The mixing ratios of CO_2 obtained from the measurements made in the air near the ground and in the atmospheric column have the following discrepancies:

- The variations of the near-surface CO_2 mixing ratios are several times higher than the variations of the column values, which confirms a weak effect of local ground-based carbon dioxide sources and sinks on the measurement results obtained in the atmospheric column;
- In summertime, the column-mean CO_2 is always lower than the mixing ratios near the ground;
- The summer minimum of the near-surface CO_2 mixing ratio leads the total column CO_2 by about a month, and the amplitude of the near-surface CO_2 is twice as large as the column amplitude.

Methane. A comparison of CH_4 mixing ratio measurements made with the use of both methods has shown that:

- Column-mean CH_4 mixing ratios do not have daily trends and vary insignificantly from day to day, reflecting a weak effect from local ground-based sources.
- Minimum near surface CH_4 mixing ratios are on the whole in agreement with the column-mean data.
- Seasonal variations of CH_4 mixing ratios according to the measurement data obtained by the two methods are in good agreement in phase and in amplitude.

Carbon monoxide. A comparison of CO mixing ratios shows that typical anthropogenic sources (traffic, etc.) do not strongly affect the column mean CO. Only during periods of fires (the second half of 2002) an increase of CO concentrations was registered not only in the air near the ground but throughout the troposphere as well. The characteristics of CO mixing ratio seasonal oscillations (phase and amplitude) are in agreement.

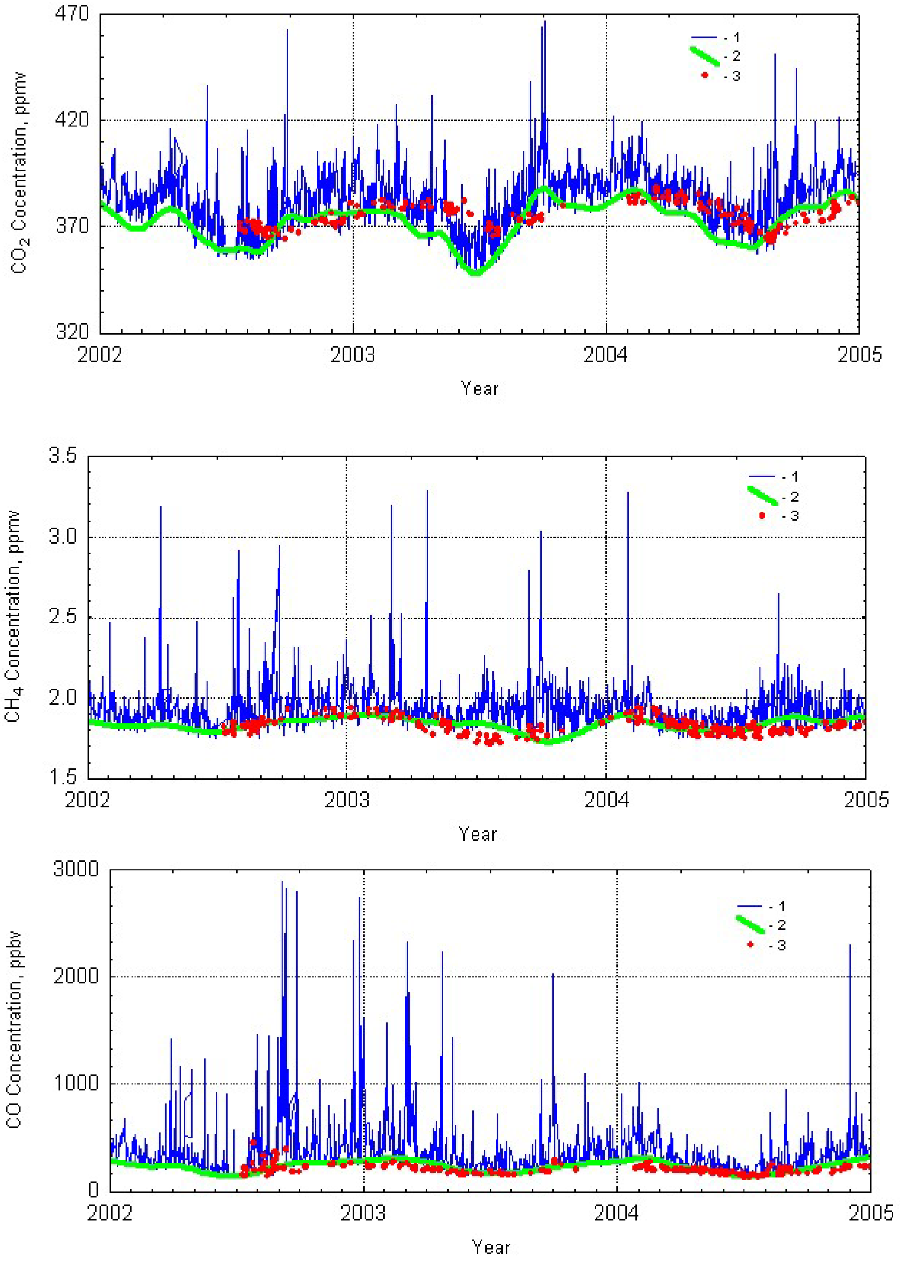

Figure 3: **Comparison of CO_2, CH_4 and CO Contents in Air near the Ground (1,2) and in the Atmospheric Column (3).**

4.2.4 Conclusions

- The results obtained reflect the spatio-temporal variability of CO_2, CH_4 and CO mixing ratios in the air near the ground and in the atmospheric column.
- Seasonal variations of CO_2, CH_4 and CO mixing ratios found during measurements made in the air near the ground and in the atmospheric column are in qualitative agreement, but a difference is observed in phases and amplitudes of these variations.
- The differences in the measurement results of CO_2, CH_4 and CO contents obtained by both methods are for the most part caused by the effect of local ground-based sources and sinks of these gases.
- Measurements of CO_2, CH_4 and CO in the air near the ground and in the atmospheric column makes it possible to obtain additional information on vertical distributions of mixing ratios of these gases in the atmosphere. Thus, it would be reasonable to measure column mixing ratios of CO_2, CH_4 and CO at the continental monitoring stations where near-surface measurements are currently made.

Acknowledgements

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4.3 Intercomparisons of Optical and in Situ CO_2 Measurements

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4.3.1 Motivation

Column measurements of CO_2 mixing ratio have become more popular recently due to development of satellite technique. Such spectroscopic CO_2 measurements from the ground have been performed continuously since 1981 over a mountainous region of Central Asia at Issyk-Kul station (42.6 N, 77.0 E, 1650 m a.s.l) Analysis of ground-based optical data usually supposes a constant mixing ratio in the entire atmospheric column. In this study we have made a statistical analysis of aircraft and surface measurements of CO_2 mixing ratio over the US Rocky Mountains from 1992 – 2002 at latitudes close to that of the Issyk-Kul station. A statistical method of data analysis using non-equidistant aircraft measurements was developed. The analysis shows that despite variability of individual vertical profiles, the average characteristics of CO_2 mixing ratios and their annual variations show only a small height variability in the troposphere over well mixed mountain regions. Therefore, the hypothesis of well-mixed columns should be valid for the analysis of the average characteristics from column CO_2 data over mountainous regions. A comparison of Issyk-Kul spectroscopic data with US aircraft and surface measurements shows satisfactory agreement. Some differences were obtained possibly owing to regional differences between mountain regions of Central Asia and the US Rocky Mountains. The comparison of column and *in situ* CO_2 measurements will allow further validation and justification of the analysis techniques.

4.3.2 Introduction

Currently, most CO_2 monitoring sites use air samples taken in flasks in the atmospheric boundary layer for subsequent measurement of CO_2 mixing ratio. For monitoring of total CO_2 content in the entire atmospheric column, spectrometric measurements of absorption of solar infrared radiation may be used. Such spectroscopic measurements are necessary also for validating existing and future satellite measurements of CO_2 mixing ratio. Therefore, validating and improvement of the main assumptions used in spectroscopic CO_2 studies are of interest.

Spectroscopic measurements of CO_2 contained in the atmospheric column have been made since 1980 at the Issyk-Kul station (Kyrgyzstan). The station is located at the bank of Issyk-Kul Lake at altitude 1650 m a.s.l. in the mountain region of the North Tien Shan of Central Asia (42ºN, 77ºE). Description of the spectroscopic method and further references are described by Kashin *et al.* (2000). One of the main aspects of the method is the assumption of constant CO_2 mixing ratio at all altitudes in the atmosphere. However, there are indications that CO_2 mixing ratio and its seasonal variations may be different at different altitudes (Keeling et al., 1968; Bolin and Bishop, 1970; Tanaka et al., 1987). Therefore, further studies of altitude variations of CO_2 mixing ratio are required.

In this report we analyze vertical changes of CO_2 mixing ratio and its seasonal variations in the troposphere from flask aircraft measurements above Carr, USA (40° 22' N, 104° 17' W) from 1992 – 2002. These measurements are made downwind of the Rocky Mountains at approximately the same latitude as Issyk-Kul station. Therefore, one may expect similar dynamic conditions over Carr and Issyk-Kul, at least for average over 10 years characteristics. The results are compared with column CO_2 measurements and surface data for sites close to Carr and Issyk-Kul station.

4.3.3 Individual CO_2 Profiles

Aircraft measurements of CO_2 mixing ratio over Carr (Colorado, USA) are made between 2 and 8 km using chemical analysis of air collected in flasks. We analyzed more than 300 vertical profiles obtained during years 1992 – 2002. Figure 1 shows examples of individual aircraft CO_2 vertical profiles. One can see variability of the profiles. Substantial vertical CO_2 changes (left plot) or near constant its mixing ratio (right plot) may occur depending on weather conditions and transport of different air masses to the observation site.

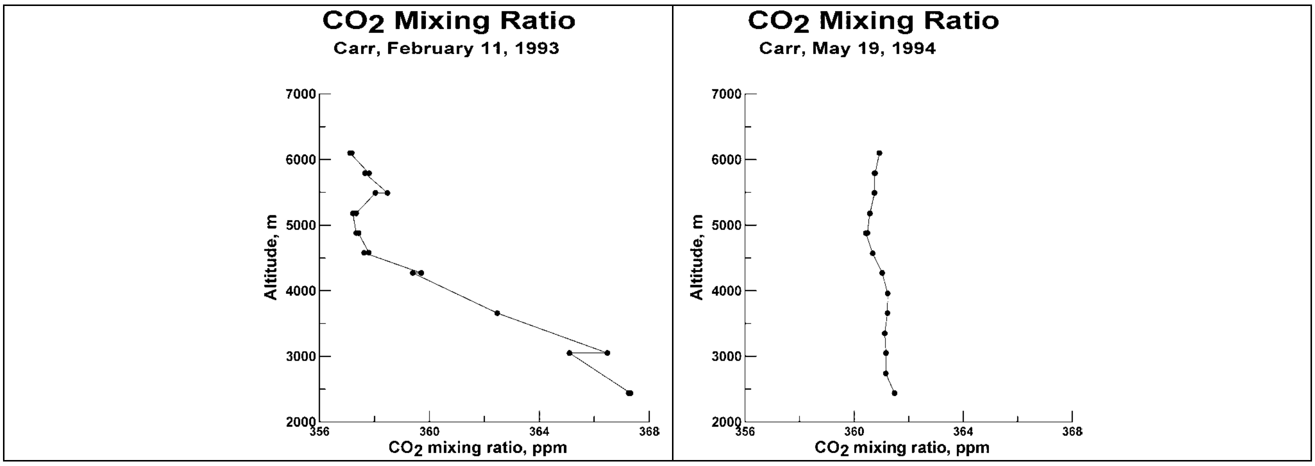

Figure 1: **Examples of vertical profiles of CO_2 mixing ratio measured with airplanes at Carr.**

4.3.4 Average CO_2 Profiles

A problem for calculating multiyear average CO_2 mixing ration and time trends may be caused by substantial variability and seasonal variations, which should be filtered out. For estimating mean characteristics from 10-year non-equidistant airplane measurements in 1.5 km thick layers we first calculate and subtract least-square fits to a linear polynomial. Then, average 2-year, annual, semi-annual, 8- and 6-month harmonics are calculated for entire 10-year interval using least-square approximation. This average seasonal variation is subtracted from the data for each altitude layer. Then, average values and the linear trend are corrected using this filtered data after extraction of outliers.

Mean values and trends of the CO_2 mixing ratio are shown in Figure 2. Amplitudes and phases of its annual harmonic are presented in Figure 3. One can see that differences between the mean CO_2 mixing ratio at different altitudes in Figure 2 does not exceed 1 ppm (and 0.5 ppm above altitude 3 km). Differences in CO_2 trends at altitudes 3 – 6 km in Figure 2 are not larger than 0.5 ppm. Larger differences in trends above 7 km in Figure 2 may be connected with lack of data before year 1995 at these altitudes.

Amplitudes of the annual harmonic in Figure 3 have small changes and are around 3 ppm at all altitudes in Figure 3. The phase of annual harmonic decreases gradually by about 20° from altitudes 2 – 2.5 km to 6 – 8 km in Figure 3. This means that maxima and minima of annual variation of CO_2 mixing ratio occur about 20 days earlier at smaller altitudes than at higher tropospheric levels.

Figure 4 shows average seasonal cycles of CO_2 mixing ratio by altitude obtained from GLOBALVIEW for airplane measurements over Carr and Poker Flat and from ground flask measurements at nearby sites Niwot Ridge and Barrow. Comparison of the left and right plots in Figure 4 reveal larger vertical changes of amplitudes and phases of the seasonal variations over Poker Flat than for Carr. But the main changes of time of the CO_2 minimum for Barrow and Carr occur below 2.5 km. Above this altitude amplitudes and phases over Poker Flat are more stable than those for Carr (see Figure 4). This may reflect a larger influence of local CO_2 sources and sinks in the boundary layer than in the free troposphere above.

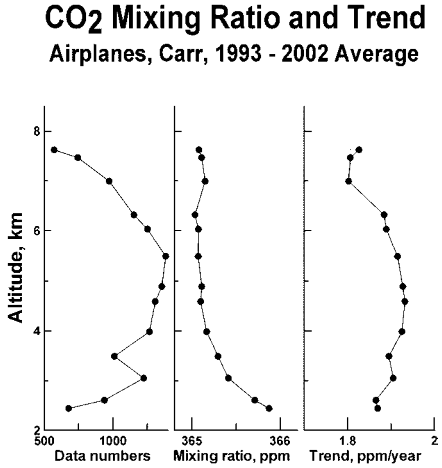

Figure 2: Numbers of airplane measurements within 1.5 km thick altitude layers at Carr (left) and average CO_2 mixing ratio (middle) and trends (right) for years 1993 – 2002.

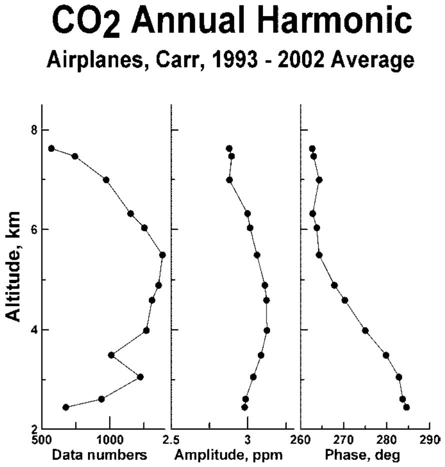

Figure 3: Same as Figure 2, but for amplitude of annual harmonic (middle) and its phase (right) of CO_2 mixing ratio averaged over years 1993 – 2002.

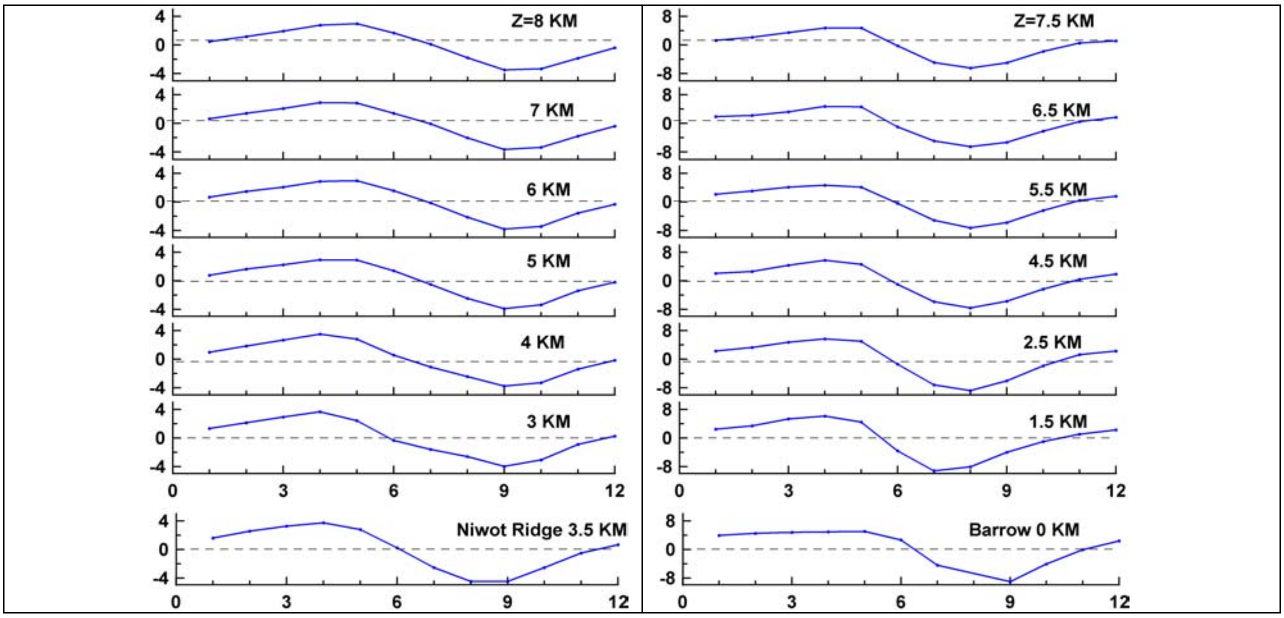

Figure 4: Seasonal variations of CO_2 mixing ratio over Carr (left) and Poker Flat (right) from airplane and ground data.

4.3.4 Interannual Variations

To analyze time variations of CO_2 trends we use the following method: The trend is calculated as the low-frequency part of the spectrum of CO_2 variations. Figure 5 shows measured CO_2 mixing ratios and their trend components obtained from Carr airplane data and from surface and column CO_2 measurements. One can see the similarity of variations at different altitudes.

Figure 6 shows detrended seasonal CO_2 variations in different years. Comparison of seasonal variations over Carr and surface data from Niwot Ridge and Utah show their similarity with larger amplitudes for surface variations (see Figure 5). Seasonal variations observed at Issyk-Kul station generally correspond to those over Carr in Figure 6. This shows that column measurements mainly reflect CO_2 variations in the free troposphere. Amplitudes of surface CO_2

variations at the Kazakhstan stations are substantially larger than those over Issyk-Kul and over Carr (see Figure 5).

Differences between surface and free-tropospheric CO_2 variations may be connected with larger dependencies of surface data on local CO_2 sources. Differences of these sources in different regions may explain larger amplitudes of surface variations of CO_2 mixing ratio in Central Asia compared to the USA (see Figure 6). Column measurements at the Issyk-Kul station give information about column CO_2 content including contribution from low altitudes. This may explain some discrepancies between Issyk-Kul and Carr seasonal variations in Figure 6. But generally seasonal amplitude variations at Issyk-Kul station are close to those in free troposphere over Carr.

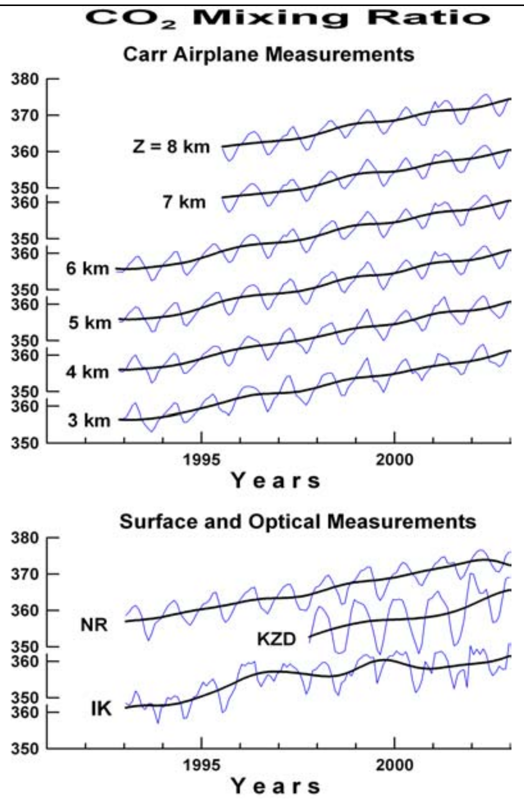

Figure 5: Observed CO_2 mixing ratio (thin lines) and low-frequency trend (thick lines) from airplane observations at different altitudes over Carr (top) and from surface measurements at Niwot Ridge and Kazakhstan, also from optical measurements at Issyk-Kul station (bottom).

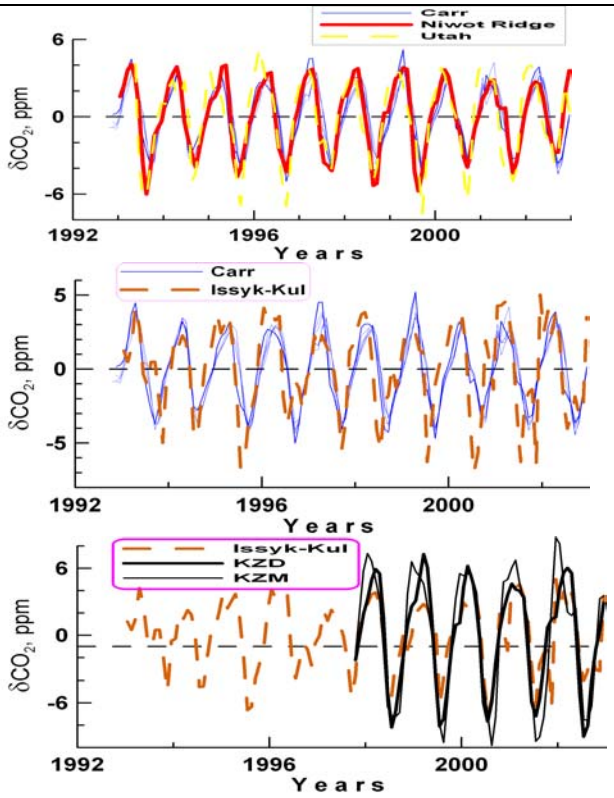

Figure 6: Comparisons of seasonal variations of CO_2 mixing ratio obtained from airplane observations at Carr and surface observations at Niwot Ridge and Utah (top), from airplane observations at Carr and Optical observations at Issyk-Kul station (middle), also Issyk-Kul data with surface measurements at Kazakh surface stations (bottom).

4.3.5 Conclusion

Statistical analysis of airplane, surface and column CO_2 measurements over the US and Central Asia between 1992 – 2002 shows the following:

- General trends and seasonal CO_2 variations are almost the same at all altitudes between three and eight km in the well mixed region just downwind of the Rocky Mountains.
- Surface and low-altitude CO_2 variations show a larger dependence on local conditions.
- Optical measurements give information about CO_2 variations mainly in free troposphere, which are more homogeneous over the globe.

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4.4 Carbon Dioxide and Other Trace Species High Precision Measurements over Amazon Basin

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4.4.1 Introduction

This project is part of the LBA project (Large-Scale Biosphere-Atmosphere Experiment in Amazônia), called "Vertical profiles of carbon dioxide and other trace gas species over Amazon basin using small aircraft". Since December 2000, vertical profiles of CO_2, CH_4, CO, H_2, N_2O and SF_6 have been measured above central Amazônia (Over Tapajós National Forest, a primary forest in Para State and over Cuieiras Biological Reserve, a primary forest in Amazonas State) and the Brazilian coast (Fortaleza over the ocean). Samples are collected aboard light aircraft between the surface and either 4 km (Tapajós National Forest) or 5 km (Fortaleza) using the NOAA/ESRL semi-automatic portable flask package (PFP). The PFPs used consist of 17 glass flasks with 750 mL volume that are pressurized to about 3 bar to enable measurements of all the gases mentioned above. Until the end of 2003 the PFP's were sent from Boulder, Colorado to Brazil, where they are filled, and then sent back to Colorado for analysis. The strategy was changed to increase the frequency of measurements, which was severely hampered due to problems inherent in shipping samples between Brazil and the United States. In order to accomplish this, a replica of the NOAA/ESRL trace gas analysis system was constructed and installed in Instituto de Pesquisa Energeticas e Nucleares/Laboratorio de Quimica Atmosferica (IPEN/LQA) starting in May 2004. The equipment set up in Brazil is capable of high-accuracy and high-precision measurements of CO_2, CH_4, CO, N_2O and SF_6 in the flask and PFP samples. All measurements are calibrated to internationally accepted scales. The analyses made at ESRL (Boulder) and at LQA (Brazil) are summarized in Table 1.

Table 1: Comparison between MAGICC system on ESRL/NOAA and IPEN/Brazil for Precision and stability.

Species	Precision of MAGICC/ESRL NOAA	Precision of MAGICC/Brazil LQA	Stability* of periodically tank call	Instrument Information
CO_2	0.05 ppm	0.03 ppm	0.02ppm	CO_2 Analyzer (LI-COR)
CH_4	< 1 ppb	1.9 ppb	0.76ppb	FID Chromatograph (HP)
CO	0.5 ppb	0.97 ppb	0.61ppb	CO Monitor (Peak Laboratories)
N_2O	0.2 ppb	0.26 ppb	0.15ppb	ECD Chromatograph (HP)
SF_6	0.03 ppt	0.05 ppt	0.02ppt	ECD Chromatograph (HP)

*Stability is the standard deviation found for the same tank call measured for all gases one time per week, since the system was installed.

4.4.2 Results

In Table 1 it was noted that only two gases have precision above the ESRL's precision and they are the gases for which the carrier gases have a high level of contaminants. But in both systems, an extra clean system to purify them has been developed. Nonetheless the precision is near that recommended for inter-laboratory comparability in the recommendations from the 12th WMO/IAEA Experts Meeting report. Perhaps more important than the high analytical precision is the fact that the system is designed around rigorous calibration of all measurements to references directly traceable to the scales used by NOAA/ESRL. The stability for CO_2 is shown in Figure 1.

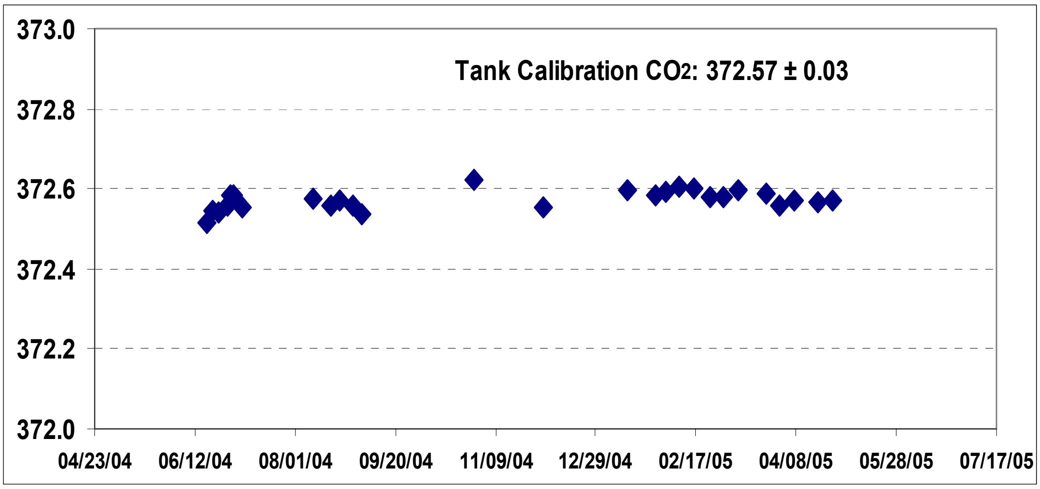

Figure 1: **Periodic tank calibrations to observe the stability of the system.**

Ambient temperature and pressure variations are normalized by using reference gases, which are measured alternately with the sample. The same procedure is also used in the construction of the calibration curves for all gases. Then all quantifications are made relative to a reference gas for each compound. For all gases, a single reference gas is alternated with the sample, except for CO_2 where we use 3 reference gases (high, medium and low mixing ratios) alternating with sample. The calibration curve for CO is made using cylinders with 7 different mixing ratios, and for N_2O the calibration curve is made with 5 different mixing ratios. For CH_4 and SF_6 only one standard and a "working" reference gas are used in the quantification. The references used for each gas are near to the concentration found in ambient, clean air. All standards and reference gases have been calibrated by NOAA/ESRL.

The results from December 2000 until June 2005 (4.5 years) show enhancement for some trace gas mixing ratios relative to mixing ratios measured at the NOAA/ESRL site at Ascension Island (7.92°S., 14.42°W, sitedode: ASC) in the tropical Atlantic Ocean (Figures 1, 2 and 3). Median CO_2 mixing ratios for single vertical profiles show a similar growth rate to the background mean at ASC, about . 1.9 ppm per year. N_2O medians show a growth rate of about 0.7 ppb/yr, also similar to the that at ASC, but are generally enhanced significantly above background. On the other hand, CH_4 and CO (not shown) growth rates are flat over this period, but CH_4 is almost always enhanced in the profiles compared to ASC. There is considerable seasonal variability observed in the ,mixing ratios. This variability for CO is very strong, where the lower concentration is 66ppb (wet season) to 240ppb (dry season). In 4.5 years the SF_6 mixing ratios (not shown) exhibit growth rate of about 0.2 ppt/yr, similar to the global trend.

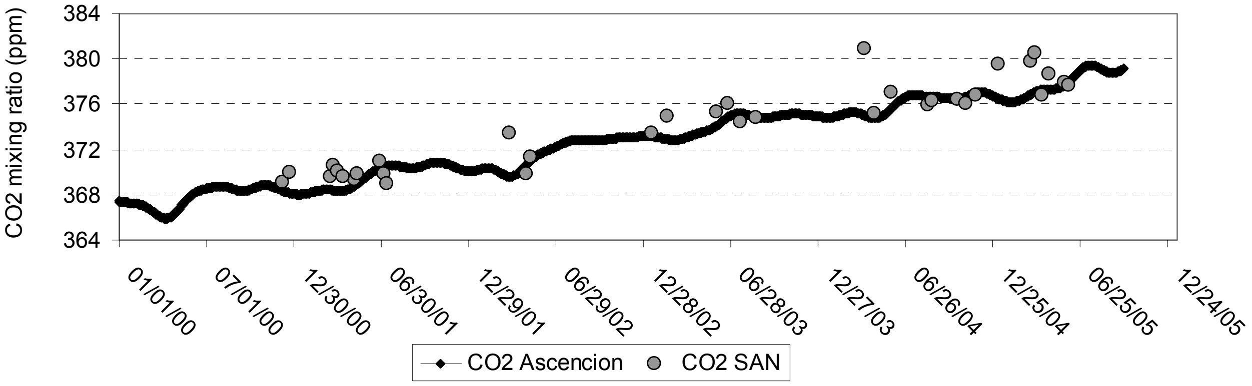

Figure 2: **Comparison of median vertical profile values of CO_2 at Santarém (SAN) and interpolated values from Ascension Island.**

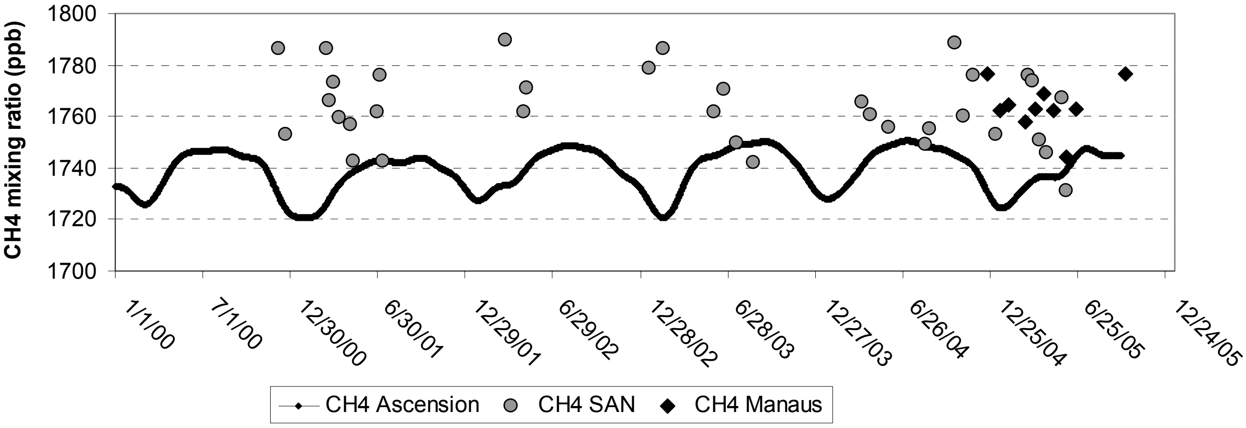

Figure 3: As Figure 1, but for CH_4, and diamond symbols represent recent Measurements in Manaus in the central Amazon.

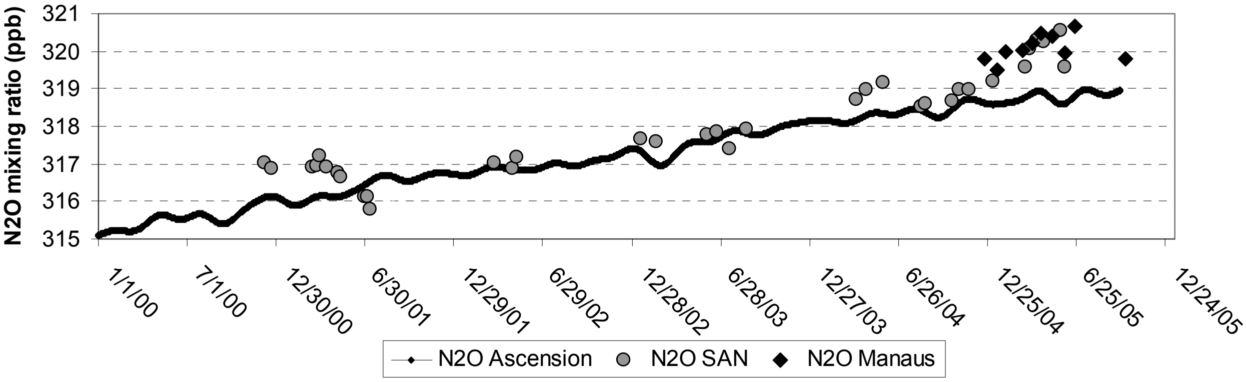

Figure 4: As Figure 2, but for N_2O.

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4.5 The CHIOTTO Tall Tower Programme In Europe: First Results

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4.5.1 Summary

The CHIOTTO project objective is to build a network of 8 tall towers on the European continent for the observation of greenhouse gas mixing ratios. In 2005 most of the eight tall towers of the CHIOTTO project came into operation. The project is part of the CarboEurope cluster of projects and will be continued as part of the atmospheric component of the CarboEurope Integrated Project (CE-IP).

Most towers are equipped with instrumentation following a standard list of recommended equipment. Calibration of the instrumentation is performed by using a set of four calibration cylinders per tower produced by the central spiking lab at MPI-BGC Jena, all calibrated using standards obtained from NOAA (tertiary standards relative to the WMO primary scale). Furthermore each station has archive cylinders to detect long term drift in the calibration standards. It is foreseen to have inter-comparisons using three-monthly rotating cylinders.

First results of some of the towers illustrate the usefulness of the continuous datasets that the programme will provide. Results from the COMET transport model show that the diurnal variations in mixing ratios can be captured quite well by transport models, which suggests that successful inverse calculations of emissions based on tall tower mixing ratio time series seem feasible.

4.5.2 Introduction

In the CHIOTTO (Continuous High precisIOn Tall Tower Observations of greenhouse gases) project an improved infrastructure for the continuous monitoring of the mixing ratios of greenhouse gases above the surface layer on the European continent has been built using tall towers. The project is based on and extends previous and existing research projects (like AEROCARB, T-COS and TACOS).

The project objective is to create the basis for a fully operational continuous observing system in the framework of the Kyoto Protocol for the sources and sinks of the most important greenhouse gases in Europe. The species measured vary somewhat from tower to tower, but include CO_2, CH_4, CO, N_2O, SF_6, O_2/N_2, and ^{222}Rn. In addition, weekly flask samples will be collected from some towers, enabling stable isotope measurements of $^{13}C\text{-}CO_2$ and $^{18}O\text{-}CO_2$.

The top heights of the towers range from 103 to 310 m above ground level, and at most towers sample measurements will be made from several heights at each tower, allowing vertical profiles to be determined. As shown in Figure 1 and Table 1, the CHIOTTO tower network spans a longitudinal range from Scotland (3°W) to eastern Poland (23°E), and a latitudinal range from Sweden (60°N) to northern Italy (44°N). The towers used are all pre-existing towers, for the most part owned and operated by telecommunications companies. The eight tall towers and their main features are listed in table 1; their positions are shown in Figure 1.

The primary motivation for obtaining atmospheric data from tall towers is to fill existing measurement gaps in geographic locations and on spatial scales. In obtaining "background" atmospheric measurements we wish to observe and quantify relatively small, long term, synoptic scale changes from within the relatively large "noise" of both local diurnal cycles and local anthropogenic emissions. Therefore, such measurements traditionally have been made using coastal or alpine locations. However, such a sampling protocol results in a geographic bias away from mid-continental locations, compromising our ability to accurately quantify the size of, and temporal variability in, the land sources and biotic carbon sinks. Additionally, coastal atmospheric measurements sites provide data on approximately hemispheric scales, whereas eddy flux measurements, for which there is a large body of existing data, provide data on scales of the order of 1 km^2. This leaves a significant data gap on spatial scales which tall tower measurements, providing data on scales of 500 km^2 to 100,000 km^2, are able to fill.

Table 2: Main Parameters of the Eight CHIOTTO Tall Towers.

		Height	Position		Mixing ratio measurement (levels)							Fluxes		
Name		(m)	Lon	Lat	CO_2	CH_4	N_2O	SF_6	CO	^{222}Rn	Flasks	CO_2	CH_4	Operator
Cabauw	NL	200	04°56’	51°58’	4	4	4	4	4	1	✓	2		ECN
Griffin	UK	232	-2°59'	56°33’	1	1	1	1	1	1				UEDIN
Hegyhatsal	H	117	16°39’	46°57'	4	1	1	1	1		✓	2		ELTE
Orleans	F	203	2°07’	46°58’	3	3	3	3	3	1	✓			LSCE
Norunda	S	102	17°28’	60°05’	4	1						2	1	LUPG
Florence	I	245	11°16’	43°49’	1	1	1	1	1					UNITUS
Ochsenkopf	D	177	11°49’	50°03’	3	3	3	3		1	✓			MPIBGC
Bialystok	PL	330	22°45’	52°15’	5	5	5	5	5		✓			MPIBGC

In addition to the motivations given above for utilising tall towers for atmospheric sampling, there are three other main strengths in creating a tall tower atmospheric measurement network such as CHIOTTO. First, CHIOTTO employs a multi-species approach, measuring not only CO_2 mixing ratios, but also a host of other greenhouse gases and related tracers. In this manner, we will obtain a much more complete picture of the carbon cycle, the processes and mechanisms controlling and influencing it, and in particular of the terrestrial carbon cycle in continental Europe. Second, we will obtain semi-continuous measurements (one sample measurement every 15 minutes or faster), allowing us to observe processes and variability occurring at high temporal frequency. For example, we will be able to accurately determine diurnal variability in the species measured. Finally, although a limited number of tall tower measurements have been made before [Bakwin et al., 1997; Bakwin et al., 1998; Bakwin et al., 1995; Hurst et al., 1997], CHIOTTO represents the first-ever network of tall tower atmospheric measurements run by a single consortium. It is this third strength which this paper aims to exploit to full advantage.

An important objective of CHIOTTO is the establishment of high quality calibrations for existing and new atmospheric measurement stations, and the implementation of a near-online data transmission system for tall tower measurements. The inter-comparability of the mixing ratio measurements between the institutes operating the air sampling networks is monitored closely. The setup chosen in CHIOTTO here was discussed at length in Manning (2003).

Calibration is secured by a three-tier approach. Firstly all stations employ a set of four ambient air working standards in high pressure cylinders, at mixing ratios spanning the expected ambient range, produced in the central spiking lab. These working standards are calibrated with high precision against NOAA CMDL standards. The calibrations of the instruments at the tower sites are performed at a frequency of least daily. The second tier is calibration using a set of three so called archive standards, also produced at the central spiking lab, at much lower frequency (once per month), to detect eventual (slow) drift in the working standards over time when the pressure in the cylinders drops. The third tier is employment of travelling standards, also produced in the central lab, that circulate along the towers every three months, in order to detect and monitor possible systematic offsets between stations. Before the end of their lifetime the working standards are to be recalibrated at the central lab. This calibration scheme is used at all towers alongside the usual setup using target, reference and zero tanks. Besides this setup each tower site is encouraged to have a set of NOAA CMDL standards and to join other inter-comparison exercises like those organised by WMO-GAW.

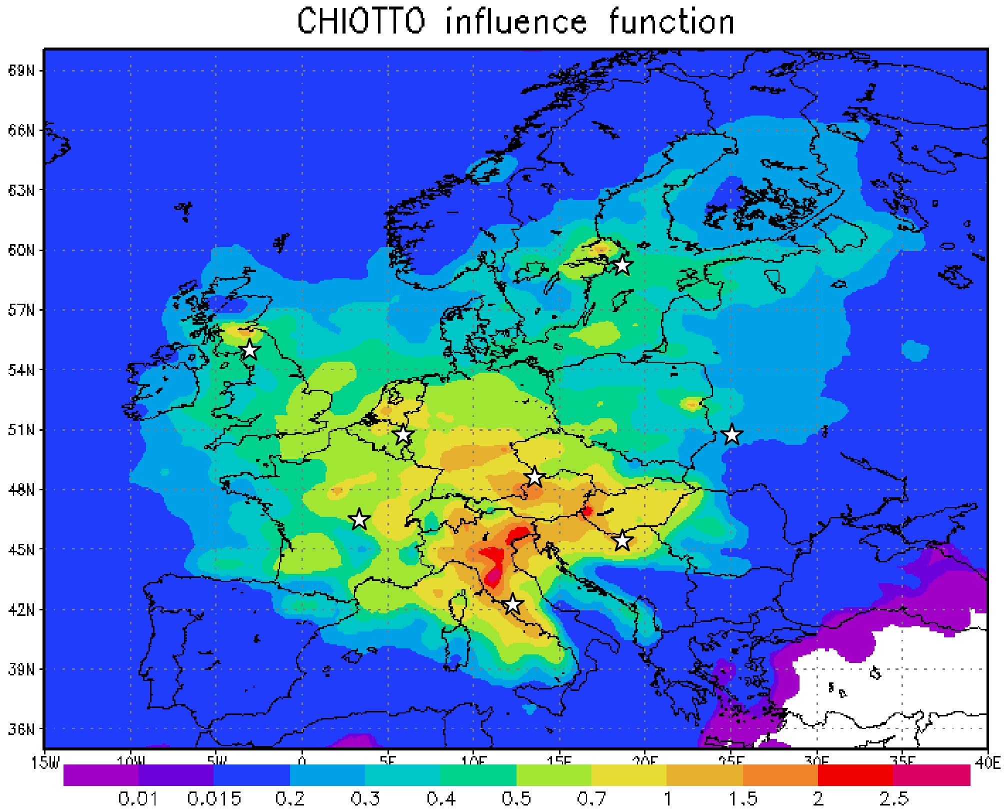

Figure 1: **The influence function for the year 2002 of the 8 CHIOTTO tall towers derived by the COMET trajectory model. The locations of the 8 tall towers are marked with the white stars. Units of the influence function are ppb/(gm^{-2}s^{-1})**

Quality controlled atmospheric mixing ratio, CO_2 flux and additional meteorological data is archived in a data centre accessible to the scientific community through the World Wide Web at the Max Plack Research Database that also houses the CarboEurope IP central database (https://www.bgc-jena.mpg.de/). Existing flux towers in the vicinity of the tall towers are integrated with the atmospheric station network in a synergetic approach enabling the tall towers to become atmospheric monitoring sites for use in transport models. Essential for the use of the CHIOTTO observations will be that air pollution transport models are applied and improved so that the information content of the mixing ratio observations can actually be used to derive improved estimates of the greenhouse gas emissions as functions of time and space. In this paper we will show that the COMET transport model (Vermeulen et al., 2001), though relatively simple in its setup compared to more traditional high resolution Eulerian models, is performing well in this respect.

4.5.3 Model Method

The COMET (CO_2 MEthane Transport) model is a Lagrangian model that can be used for both predictive and inverse modelling purposes. COMET uses backward trajectories. The calculations described in this paper were performed using trajectory and mixing layer height data derived from 1 by 1 degree, 3 hour resolution ECMWF analysed meteorological data. The hourly 3D 96 hour backward trajectories were calculated from analyzed wind fields using the Flextra programme (Stohl et al., 1999).

In the COMET model two vertical layers are distinguished, a mixing layer and a reservoir layer. The initial methane mixing ratio at the start of each trajectory is taken in this case from the two-weekly averages of the calculated methane mixing ratios of the TM2 global tracer transport model (Heimann, 1995) for 1995. The height of the mixed layer in contact with the surface varies as a function of time. All emissions are accumulated in this mixed layer. When the mixed layer height changes mass transfer takes place with the second layer, called the reservoir layer. The area that exchanges emissions with the column of air in the mixed layer is circular and the diameter of this circle changes linearly with travel time from large at the start of the backward trajectory to small at the destination. A more detailed description of the COMET model can be found in Vermeulen et al. (1999, 2001).

In forward mode the COMET model retrieves per time step the emissions for the grid cells under the current circular source area and calculates the mixing ratio changes and isotopic composition for the modelled components in the column of air with the current mixing layer height. Mixing layer heights are estimated from the 3D ECMWF data using a critical Richardson number approach ($RI_c=0.25$). Emission data is retrieved from emission inventories per source category on a regular grid; for methane the high resolution (10 minutes lon/lat and 3 hours in time) METDAT database (Berdowski et al., 1998) is used, and the base year for the emissions in METDAT is 1995.

4.5.4 Measurement Results

In the 1st year of the CHIOTTO project we have defined the requirements for the equipment to be used as well as the measurement, calibration and data submission protocols. The choices made here concerning the calibration protocol are discussed in Manning (2003). These are the foundation of the project. On the basis of this information the new equipment was purchased, customized and installed. In the 2nd year we continued to implement these choices from the 1st year, building instrumentation with all modifications required to meet our specific and high demands regarding quality and materials.

The CHIOTTO project is at the time of this writing in its 3rd and final year and all towers, except Orleans, are now operational in the new setup. The CHIOTTO mixing ratio data will be used, for example, in CarboEurope-IP in attempts to derive estimates for the strengths of CO_2 sources and sinks of Europe, in combination with other measurements and other global and regional networks. The CHIOTTO tall towers will form an integral part of the CarboEurope IP (CE-IP) as one of the activities of the Atmospheric Component. CE-IP officially started in January 2004 and will continue until December 2008.

In Figure 2 an example time series for the mixing ratio gradients of CO_2 , CH_4, N_2O and SF_6 measured at the Cabauw tower is shown together with the ^{222}Rn observations. Figure 2 shows that the high measurement precision and time resolution, combined with the vertical gradient, reveal a lot of variation and thus information. The diurnal variation is most clear at the lower measurement levels with higher night time mixing ratios in this period up to 430 ppm for CO_2. The highest measurement level is usually less affected by the night time peaks but shows day to day variations in this period between 380 and 420 ppm. The most prominent feature of the higher level measurements in this period are the early morning peaks, when the emissions built up during night time inversions passes the measurement level during the break-up of this inversion layer in the early morning between 6 and 10 UTC.

The importance of generating long time series of observations is illustrated by the analysis of the data shown in Figure 3. At Cabauw tower, observations of CO_2 and CH_4 gradients have been performed since 1993. Figure 3 shows the CO_2 mixing ratio at four levels for the four year time period 2000-2004. As in Figure 2 we can see the lower and less variable mixing ratios at the highest level (200 m AGL) and the highly variable mixing ratio at the lowest level (20m AGL). All levels show a clear seasonal pattern with highest mixing ratios in winter and lowest mixing ratios in summer. When using only the average daytime values from the highest measurement level and by applying a least-squares harmonic fit with time periods of 1 and 0.5 year and a linear trend in time, the mean annual growth rate for CO_2 at Cabauw can be calculated to be 2.5 $ppm.yr^{-1}$. The best fit shows a good correlation between model and observations, $R^2=0.73$.

This analysis of the data in Figure 3 illustrates that even for a tall tower like Cabauw, though surrounded by extensive areas with (local) sources and sinks, detection of the global growth rate and the latitudinal seasonal variation for CO_2 is possible by using day time well mixed conditions and mixing ratios from the higher levels of the tall tower.

The correlation of measured hourly mixing ratios of CO_2 and CH_4 is very high with $r^2 = 0.85$. This is mainly due to the same diurnal pattern for both species. The seasonal pattern, however, is quite different for these species, with a relatively small and less defined amplitude of the seasonal variation for CH_4 of 80 ppb (4%) compared to that for CO_2 (26 ppm=7%). The growth trend in methane mixing ratio at Cabauw was even negative over the period 2000-2004 with a value of -1.3 +/- 1.0 ppb.yr^{-1}.

Other greenhouse gases like N_2O and SF_6 show even different behaviour, but as the time series of these gases have just started for the CHIOTTO tall towers, similar analyses could not be performed yet. However, figure 4 illustrates the different behaviour of these two species compared to CO_2 and CH_4 for a measurement period in September 2005 at the Cabauw tower. The N_2O mixing ratios show small vertical gradients and small accumulations in the mixed layer. SF_6 mixing ratios show small variations except for short duration events where mixing ratios can even double.

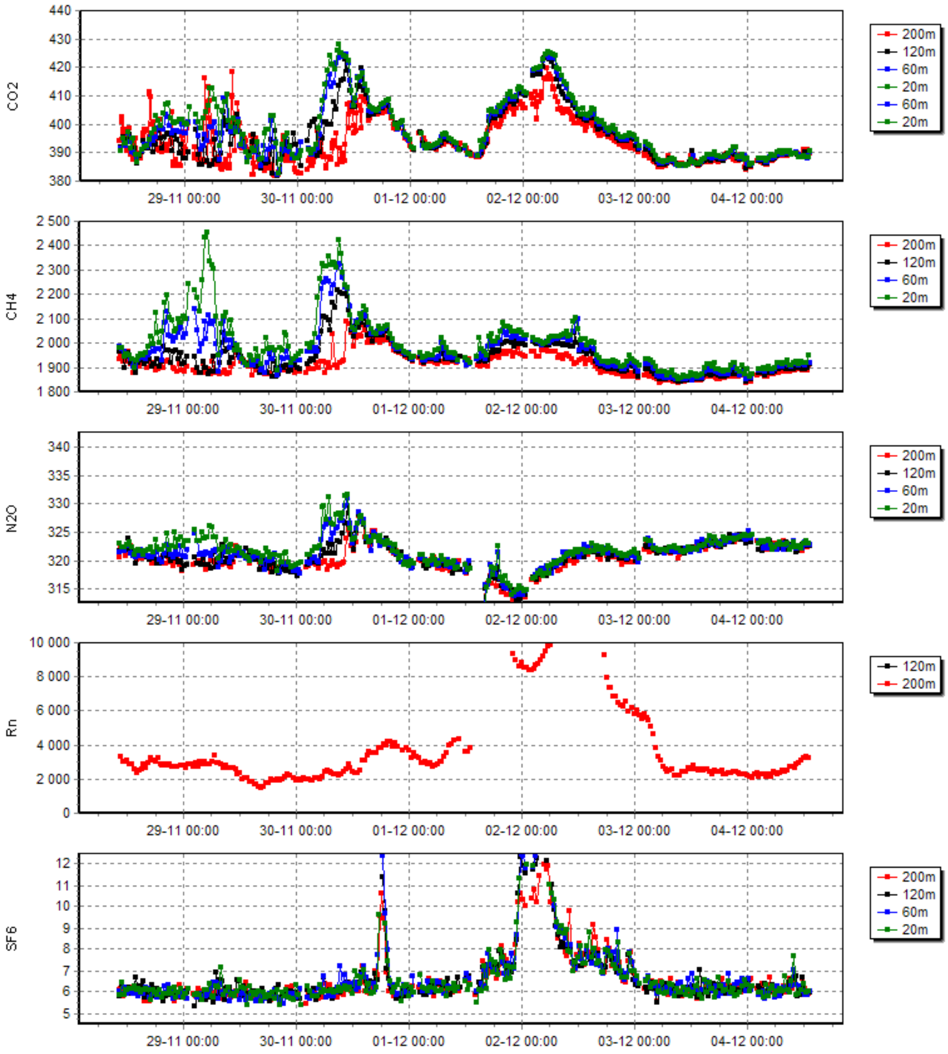

Figure 2: Vertical Mixing ratio gradients for CO_2 (ppm), CH_4 (ppb), N_2O (ppb) and SF_6 (ppt) at Cabauw (NL), 29Nov-5Dec 2005. The data shown is level 2 near-real time data not corrected for instrumental baseline drift.

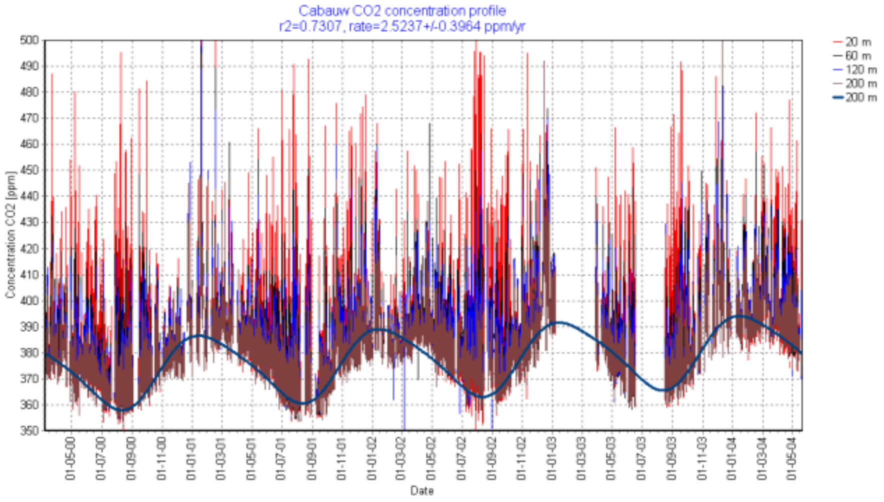

Figure 3: **CO_2 mixing ratio gradient at Cabauw (NL) in the years 2000-2004 and the detected seasonal trend estimated using regression and harmonic analysis. The growth trend for CO_2 determined in this period is 2.5 +/- 0.4 $ppm.a^{-1}$**

4.5.5 COMET Model Results

The COMET model was applied to simulate the hourly mixing ratios at Cabauw tower and Macehead (Simmonds et al, 1993) for the year 2002. The results are shown in figures 4 and 5 for Cabauw and in figure 6 for Macehead. Figure 5 shows the measured and modelled time series for a four month period. For Cabauw we calculated the mean mixed layer mixing ratio from the Cabauw vertical mixing ratio profile observations along the tower, taking into account only those observations that fall within the modelled mixed layer.

The diurnal variation in mixing ratio is captured well by the model. Both timing and height of the daily maxima and minima are realistic. Also the synoptic variation and building up of methane in high pressure anticyclonic conditions is represented well by the model. The correlation between model and measurements is further illustrated by figure 5. The COMET model explains about 67% of the variation in the measured mixing ratio, the RMS error is estimated at 2.3 ppb, which is similar to the measurement error. Overall the simulated mixing ratios (relative to the global background of 1760 ppb) are 18% higher than the observations. This could be due to systematic errors in the model or its underlying data like emissions rates and mixing layer height.

In Figure 6 the modelled and measured hourly methane mixing ratio is shown for Macehead. Here also both diurnal and synoptic time scale variation are captured quite well, although the correlation coefficient (R^2=0.48) is less than for Cabauw. This is probably due to the fact that the Macehead data is ground level data, while for Cabauw we calculated the mean mixed layer mixing ratio from the Cabauw vertical mixing ratio profile along the tower.

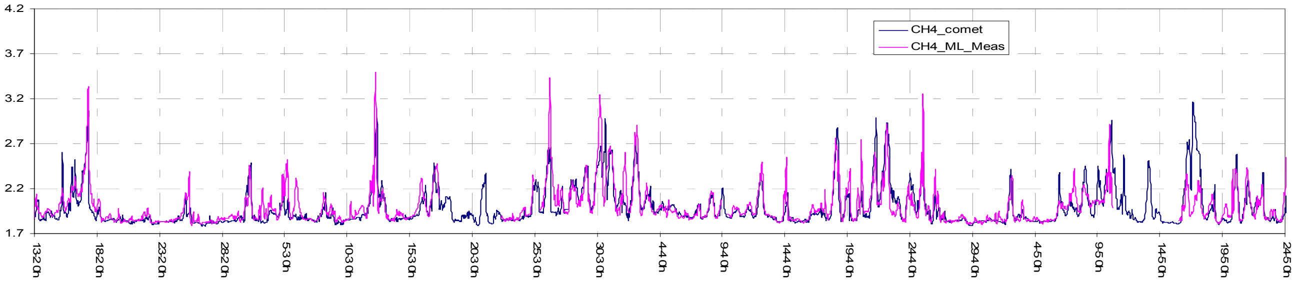

Figure 4: **Hourly mixed layer average CH_4 mixing ratio (ppm) at Cabauw, Feb-May 2002 as measured (light blue) and modelled (dark blue) with the COMET model in forward mode.**

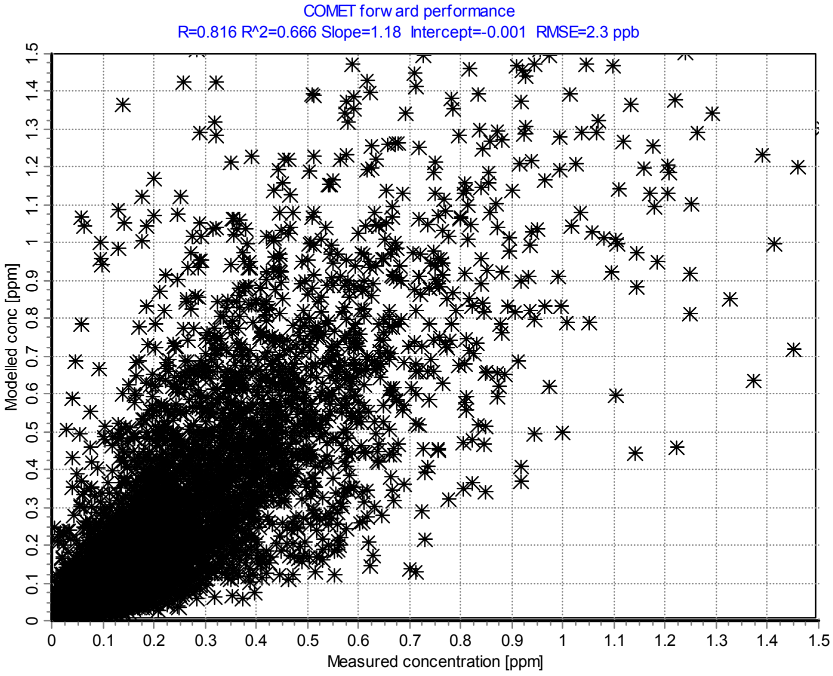

Figure 5: Correlation plot of mixed layer CH_4 column mixing ratio at Cabauw for 2002 as measured versus modelled with the COMET model in forward mode (ppm above mean background mixing ratio). R^2=0.67; model=1.18*meas+0.001; RMS error =120 ppb.

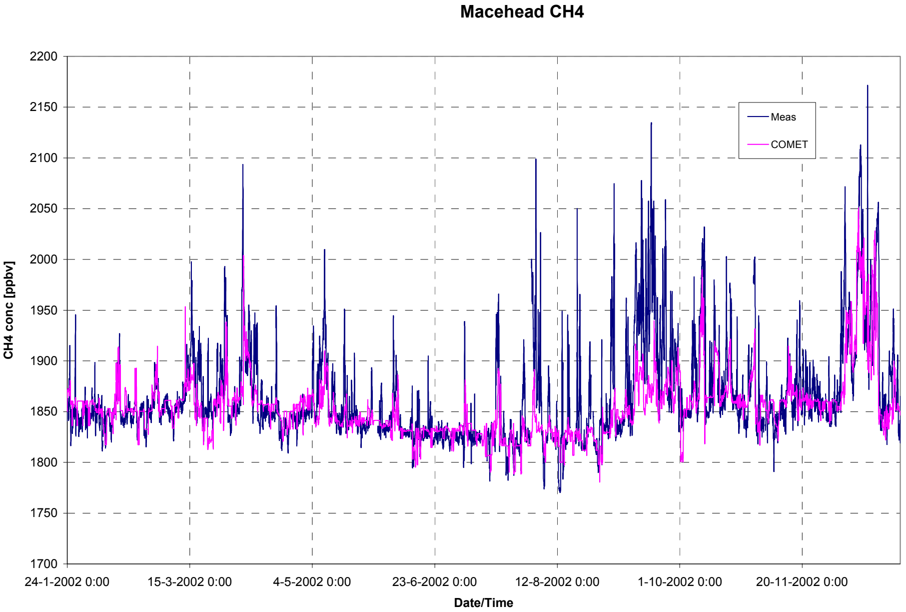

Figure 6: Macehead measured (dark blue) versus COMET (light blue) forward modelled CH_4 mixing ratios (mixing ratios in ppb, R^2=0.48).

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4.6 High Precision $\delta^{13}C$ Analysis of CH_4 and CO_2 using a Modified and Automated GV Instruments Trace Gas and its Applications

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Royal Holloway, University of London

4.6.1 Introduction

A GV Instruments Trace Gas preparation system coupled to an IsoPrime mass spectrometer (in continuous flow set-up) was installed at Royal Holloway, University of London (RHUL) in March 2003. The instruments are used for analysis of $\delta^{13}C$ of CH_4 and $\delta^{13}C$ and $\delta^{18}O$ of CO_2 in ~75 mL air samples of ambient mixing ratio. The off-the-shelf precision for methane $\delta^{13}C$ analysis is approximately 0.3‰. An instrument of this precision is useful for source studies, but clearly would not be suitable for background air measurements where the seasonal cycle may only be of the order of 0.2‰. Small-scale modifications have since been carried out to improve precision but without significantly changing the commercial product. The inlet system has been fully automated so that the system can be run semi-continuously, measuring outside air at the Royal Holloway sampling site, west of London. The developments are described in greater detail in Fisher *et al.*, 2006.

4.6.2 Calibration

The instruments have been calibrated by measurement of a NOAA CO_2-in-air standard ($\delta^{13}C$ -8.431‰) and a light CO_2 standard from IUP-Heidelberg (-50.17‰) diluted with zero air. A mass spectrometer scaling effect yielding an offset of 0.8‰ at the light end of the scale, means that measurements of methane $\delta^{13}C$ need to be adjusted accordingly. Methane $\delta^{13}C$ measurements have also been inter-compared with other laboratories as part of a round-robin for Meth-MonitEUr (an EU-funded methane monitoring consortium). An internal working standard tank of air collected at RHUL, which has been measured using a conventional NIWA-design offline extraction line and dual inlet mass spectrometer (Lowe *et al.*, 1991, Lowry *et al.*, 2001), is also analysed daily.

4.6.3 Catalyst Tests

Like most other $\delta^{13}C_{CH4}$ preparation systems, methane $\delta^{13}C$ analysis using the Trace Gas involves oxidation of the methane in an air sample to carbon dioxide which is then analysed in the mass spectrometer. The efficiency of the oxidation of methane to carbon dioxide limits the accuracy and precision of the $\delta^{13}C$ values obtained. Three catalysts have been tested in the furnace of the Trace Gas at a range of temperatures.

Braided platinum, copper and nichrome wires (Pt/Cu/NiCr) are the standard catalyst used in the Trace Gas. This catalyst required oxidation with oxygen mixed into the helium flow with the furnace at operation temperature for ~1 hour at the start of each day of analyses. There was a depletion in measured $\delta^{13}C$ for consecutive measurements of the internal working standard tank, with shifts of >1‰ over the course of 16 measurements on a particular day. Platinised quartz wool and palladised quartz wool catalysts use the oxygen present within the air sample for oxidation of the methane and daily furnace conditioning is not required. To use these catalysts the standard 0.5 mm I.D. furnace tube had to be changed to a 4 mm I.D. tube. CH_4 analysis using the platinised and palladised quartz wool catalysts did not show the depletion that was seen with the Pt/Cu/NiCr wires. Each of the catalysts were tested at a range of temperatures and an optimum temperature for each catalyst, i.e. the temperature at which peak height, accuracy and repeatability are at an optimum are determined (Table 1).

Highest repeatability was achieved using a palladised quartz wool catalyst at a temperature of 790°C. Peak heights were greater than double the height of those obtained with the Pt/Cu/NiCr wire catalyst. Flow rate of the helium through the furnace also has a large effect on the measured $\delta^{13}C$. For the palladised quartz wool a flow rate >40 mL/min was found to produce the largest peak heights and most accurate and precise values.

Table 1: Catalysts tested in the Trace Gas furnace and the optimum temperature, peak heights, and precision obtained (before addition of the automated inlet).

Catalyst	Optimum Temperature (^oC)	Peak height (nA)	Precision 1σ, n=10 (‰)
Platinum/Copper/Nichrome braided wires in 0.5 mm I.D. furnace tube	960	3.0	0.19
Platinised Quartz Wool in 4 mm I.D. furnace tube	800	2.4	0.14
Palladised Quartz Wool in 4 mm I.D. furnace tube	790	7.1	0.09

4.6.4 Automated Inlet

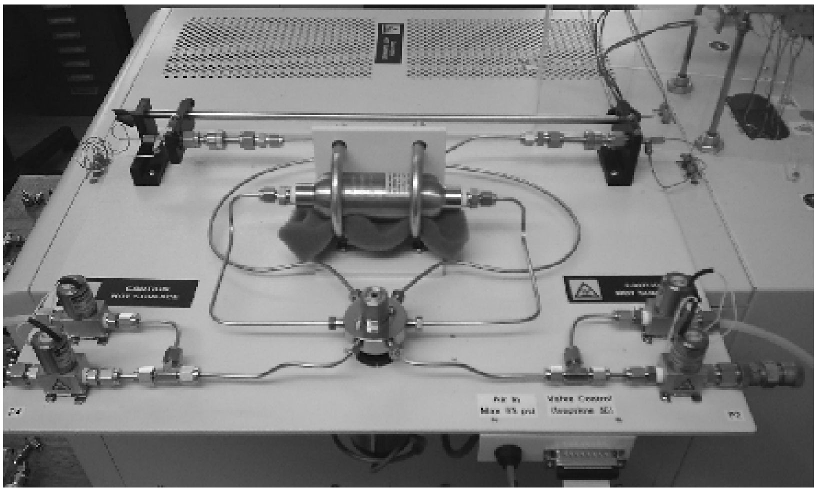

Figure 1: The automated inlet system on the Trace Gas.

Addition of an automated inlet system (Figure 1) in November 2004 means that the Trace Gas can be run semi-continuously, analysing the isotopic composition of either methane or carbon dioxide in outside air at half-hourly intervals. One of the 2-way valves is connected to a pump, continuously pumping air from an air inlet on the roof of the building. As air flushes through the sample volume the connections to the Trace Gas are purged with helium. Every half hour the 6-way valve switches and the air sample is directed into the Trace Gas for analysis. Another 2-way valve is connected to a working standard tank which is regularly analysed, usually several times at the start of each day of analyses and then at 4 to 6 hour intervals.

Addition of the automated inlet system further improved the repeatability of analyses, by removing contamination with lab air, and keeping the timings of the pumping/filling routine constant. Precisions of 0.05‰ for $\delta^{13}C_{CH4}$ and 0.03‰ for $\delta^{13}C_{CO2}$ can now be routinely achieved (1σ, n=10).

4.6.5 Diurnal Studies

At present the system is usually run overnight during high pressure, anticyclonic periods when a large build-up in concentrations of methane and carbon dioxide is expected to occur. Examples of methane and carbon dioxide diurnal studies are shown in Figs. 2 and 3. The internal working standard tank is run every 6 hours. During the diurnals shown the standard deviation in secondary standard tank analyses was 0.03‰ for $\delta^{13}C_{CO2}$ (15 analyses over 4 days) and 0.08‰ for $\delta^{13}C_{CH4}$ (11 analyses over 3 days). There is no apparent memory effect between tank analyses and outside air analyses.

The RHUL sample site is situated to the west of London, 32 km from the centre of the city. Mixing ratio and isotope analysis at 30-minute intervals allows individual source plumes to be identified as the wind changes direction. Results can be subdivided according to wind direction and Keeling plots (Keeling, 1961) are used to estimate the source signature of excess CO_2 or CH_4 over background for different sectors. For CO_2, the easterly sector (i.e. in the direction of London) has an average source signature of -30.4‰. Results from CH_4 diurnals at RHUL are strongly affected by wind direction. Wind direction was from the east on the night of the 17th-18th August (Fig. 3) and there was a depletion in $\delta^{13}C$ as CH_4 mixing ratio increased, indicating a dominance of biogenic local sources, primarily landfill sites in that sector. If the wind direction is from the west there is usually an enrichment in $\delta^{13}C$ with increasing CH_4 mixing ratio, pointing to a dominance of sources such as gas leaks. Carrying out diurnal studies throughout the year will provide information on annual variability in methane sources.

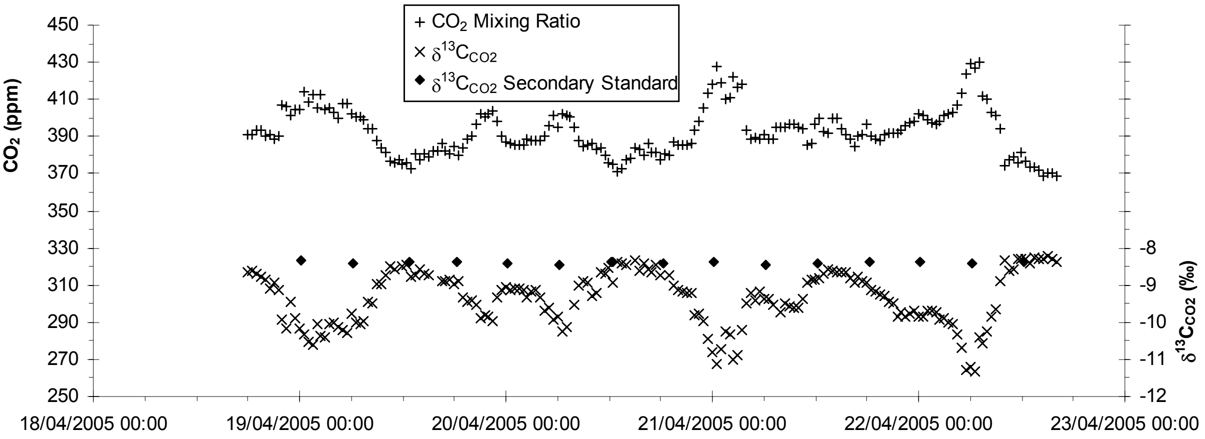

Figure 2: **CO_2 Diurnal Study, April 18th – 22nd 2005. Time series of CO_2 mixing ratios and $\delta^{13}C$ of CO_2. Secondary standard tank $\delta^{13}C$ measurements are also shown.**

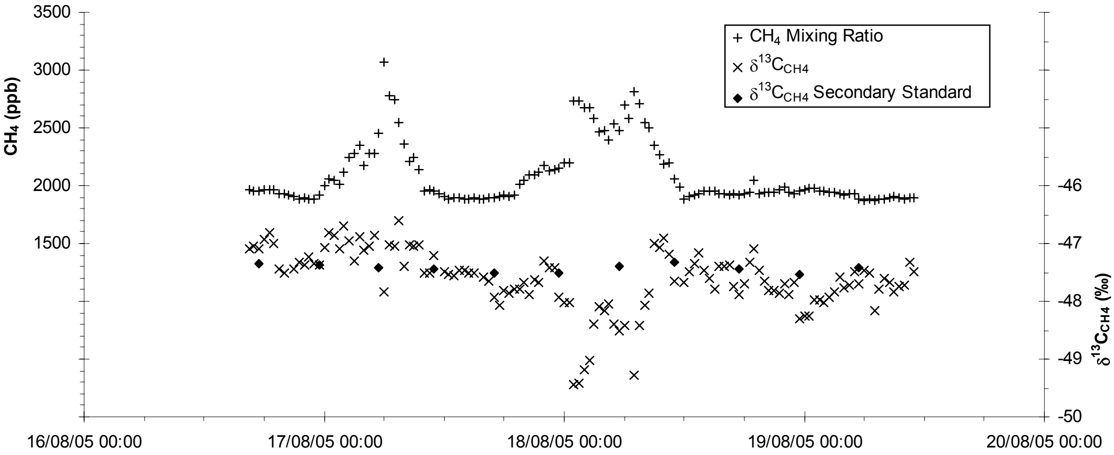

Figure 3: **CH_4 Diurnal Study, August 16th – 19th 2005. Time series of CH_4 mixing ratios and $\delta^{13}C$ of CH_4. Secondary standard tank $\delta^{13}C$ measurements are also shown.**

4.6.6 Wetland Source Studies

The small volume of air required using continuous-flow systems such as the Trace Gas makes the technique ideal for source studies. This has been illustrated by using the Trace Gas to analyse $\delta^{13}C_{CH4}$ of air collected in wetland areas in 3 L stainless steel tanks, 2 L glass flasks, and 1, 3 and 5 L Tedlar bags. Each of these has been found suitable for CO_2 and CH_4 collection for source studies. 1 L of air collected in bags was sufficient for GC CH_4 mixing ratio analysis and triplicate Trace Gas $\delta^{13}C_{CH4}$ analyses for air collected in closed chambers over the wetlands. Keeling plots for these experiments in wetlands in Ireland and Siberia are shown in Figs. 4 and 5.

Methane emissions from wetlands in Ireland are poorly quantified and are highly variable between different types of wetland (raised bogs - mainly in the midlands, blanket bogs - mainly along the west coast, and fens) and within each wetland area. Isotopic source signatures of emitted methane ranged from -57‰ to -83‰. The most isotopically depleted methane was measured in raised bogs. A Keeling plot depicting emissions from Clara bog, in central Ireland, in October 2004, indicates a source signature of -82.7‰ (Figure 4).

The West Siberian samples were collected from wetlands near Korotchaevo in September 2004. This area is part of the Ob River wetland zone but also a region of major gas fields. The source signature of the emitted methane was -65.3‰ (Figure 5).

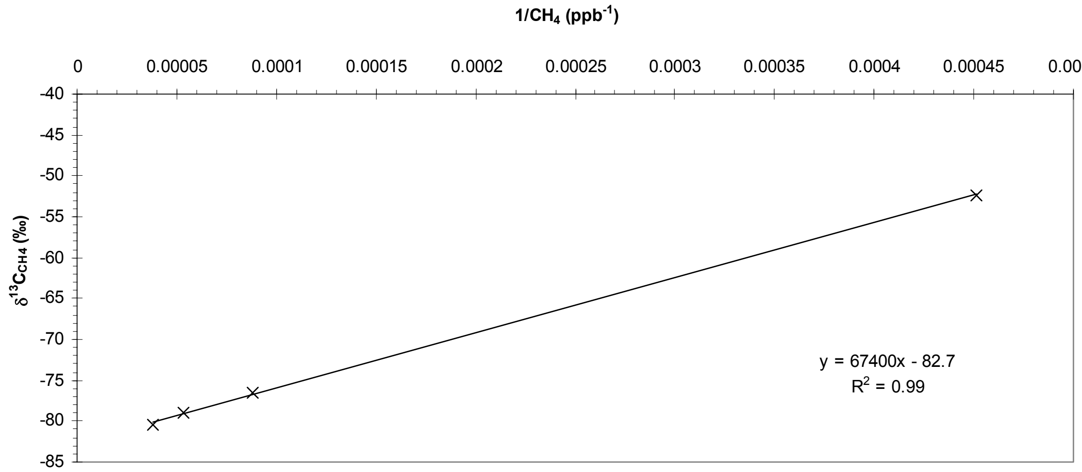

Figure 4: **Keeling Plot for CH_4 accumulated in a closed chamber over Clara Bog, central Ireland, 19th October 2004. Total accumulation time was 8 hours. Samples were collected in 1 L Tedlar bags. Average standard deviation (1σ) in triplicate analyses was 0.09‰. Samples were analysed prior to installation of the automated inlet system.**

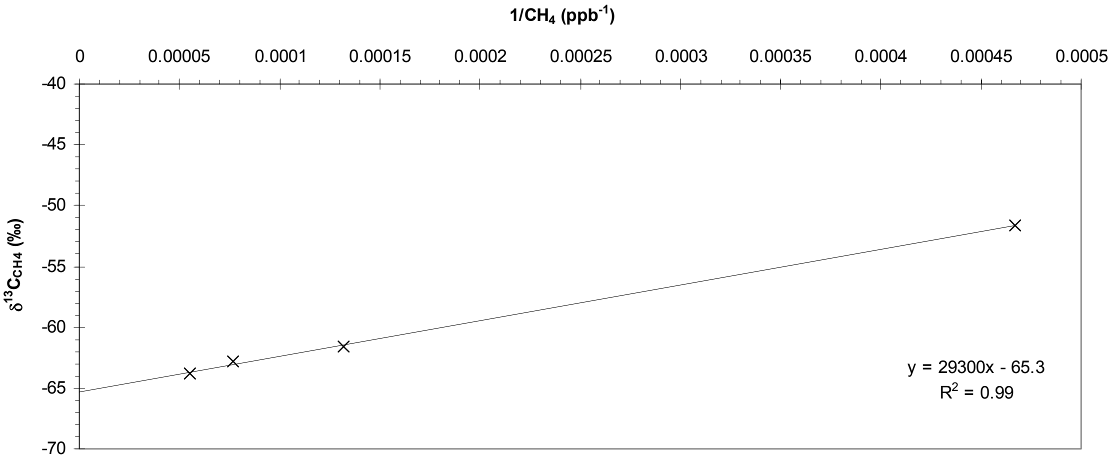

Figure 5: **Keeling Plot for CH_4 accumulated in a closed chamber over wetland near Korotchaevo, W. Siberia, 22nd September 2004. Total accumulation time was 1.5 hours. Samples were collected in 1 L Tedlar bags. Average standard deviation (1σ) in triplicate analyses was 0.07‰.**

4.6.7 Conclusion

With the addition of an automated liquid nitrogen dispenser the Trace Gas could be run for period of days without on-site assistance, obtaining a continuous half-hourly record of $\delta^{13}C_{CH4}$ or $\delta^{13}C_{CO2}$ and $\delta^{18}O_{CO2}$ of outside air. At a continental site this would provide important information of changing sources of the gases, both seasonally and interannually. At a background site a continuous record is unlikely to provide much more useful information than weekly or bi-weekly flask sampling, although it might record an event plume which would otherwise be missed. The new developments to the Trace Gas have made the instrument ideal for measuring diurnal variations at an urban site, and with the improved precision it has the potential for measuring the seasonal cycle at background stations. It can also be used for improved measurement precision of methane source samples.

Acknowledgements

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5. NATIONAL REPORTS

5.1 National Report Greenhouse Gases and Related Tracers Measurement at Waliguan Observatory, China

L. Zhou, X. Zhang, Y. Wen and D. Zhang
Centre for Atmosphere Watch and Services (CAWAS), Chinese Academy of Meteorological Sciences (CAMS), China Meteorological Administration (CMA), Beijing

5.1.1 Introduction

In the past decade, the China Meteorological Administration (CMA) has been participating actively in the WMO-GAW activities. The main contribution includes the established GAW station Mt. Waliguan (WLG) and three regional stations: Shangdianzi (SDZ), Lin'an (LA) and Longfengshan (LFS), as well as three new regional stations: Zhuzhang (ZZ), Akedala (AKDL) and Jinsha (JS) that support global networks for ozone, UV, greenhouse gases, aerosols, selected reactive gases and precipitation chemistry (Figure 1). On 16 December 2004, CMA officially announced the establishment of the Centre for Atmosphere Watch and Services (CAWAS, CMA). The CAWAS has been assigned to lead the atmospheric chemistry observations (including GAW stations in China), research and forecasting programmes of the CMA.

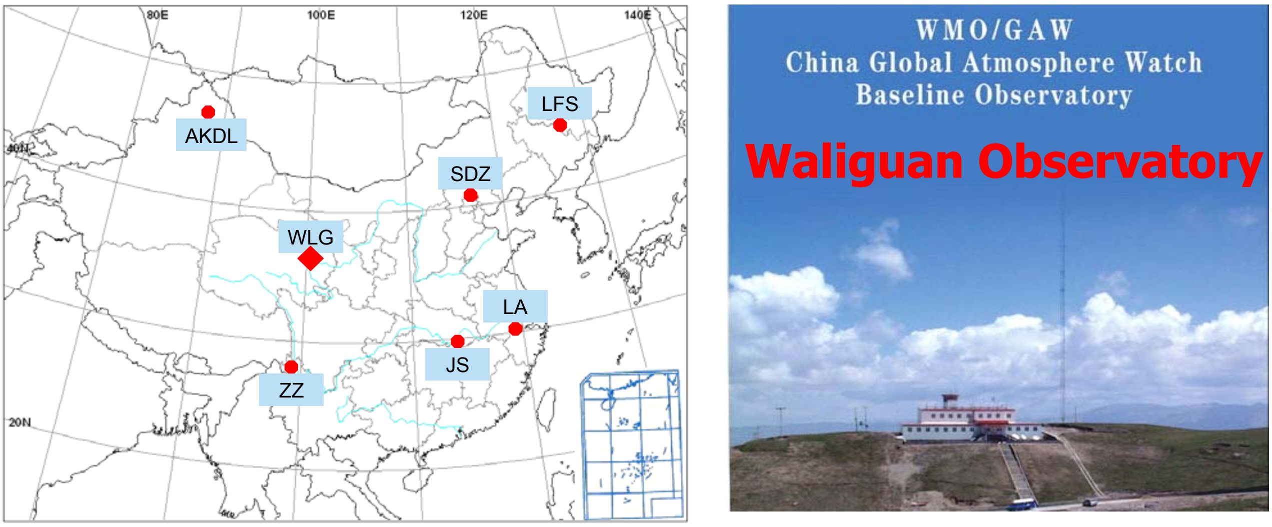


Figure 1: Geographical location of the 7 WMO-GAW Stations and in China and a photograph of the Waliguan station.

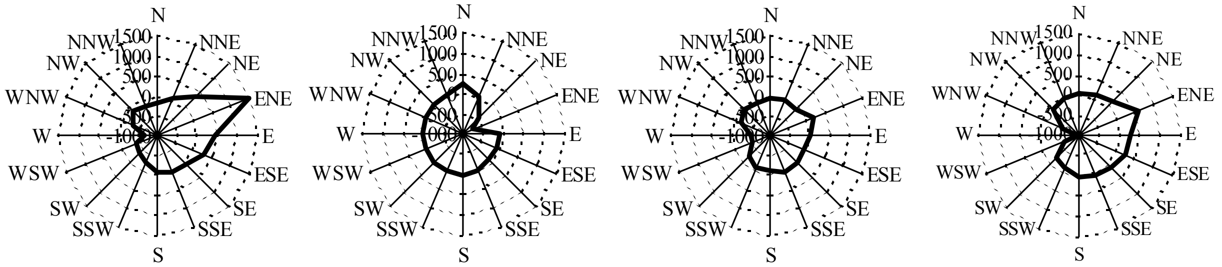
Waliguan Observatory (WLG, 36°17'N, 100°54'E, 3810m asl) is located at the top of Mt. Waliguan in remote Western China. The unique location provides an ideal platform to monitor background air as well as to conduct research in a pristine continental environment. The station offers good facilities for atmospheric research and measurement campaigns. At present, routine measurement programmes include atmospheric CO_2, CH_4, CO, NO_2, SO_2, surface ozone, total ozone & profile, black carbon, aerosol properties, radiation (global, direct, diffuse irradiance, and UV-B), precipitation chemistry and PBL meteorology. The laboratory hosts in-situ atmospheric CO_2, CH_4 and CO monitoring systems on the second floor of the main building. An 89m tower, erected 20m east of the main building, is used to measure certain meteorological parameters at different levels (10m, 20m, 40m, 80m heights) and to obtain air samples from the 80m height for the in-situ CO_2, CH_4 and CO measurements.

5.1.2 In-Situ Measurement and Discrete Sampling

5.1.2.1 In-situ Measurement and Background Data Selection

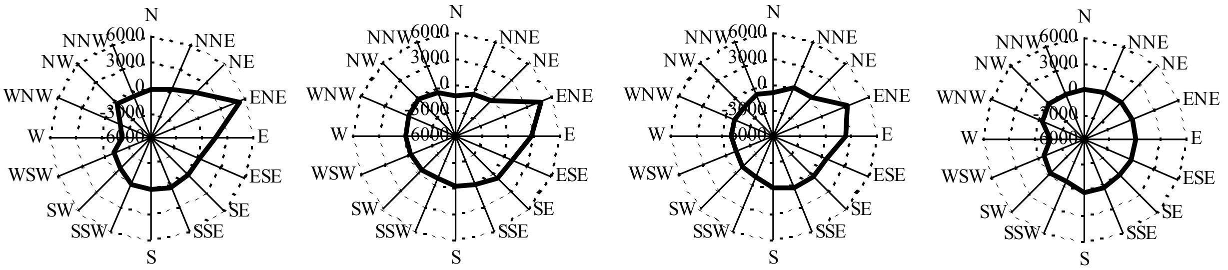
The in-situ CO_2 mixing ratio is measured using a Licor 6251 NDIR (continuously from August 1994). The in-situ CH_4 and CO_2 mixing ratio is measured by an HP5890 GC-FID (64 ambient injections per day from August 1994 to August 2001; *ca.* 170 ambient injections per day from September 2001 after a system upgrading) and the in-situ CO mixing ratio is measured by an RGA-3 (14 ambient injections per hour from November 1997).

For background data selection at WLG, the atmospheric CO_2 and CH_4 hourly mixing ratios have been segregated by horizontal wind direction/speed and vertical winds, respectively, merged by season over the entire measurement period. The background atmospheric CO_2 and CH_4 mixing ratio data selection procedures were suggested according to statistical analysis and influence of local surface winds. Selected hourly data sets representing baseline conditions account for approximately 70% and 50%, respectively, of the raw CO_2 and CH_4 records, respectively. Figures 2 and 3 present the atmospheric CO_2 and CH_4 hourly mixing ratios weighted by frequency of wind occurrence in spring, summer, autumn and winter at WLG.



Spring (CO_2 loading) Summer (CO_2 loading) Autumn (CO_2 loading) Winter (CO_2 loading)

Figure 2: **Atmospheric CO_2 "loading" in spring, summer, autumn and winter at Mt. Waliguan. Loading is defined as: (counts of hourly CO_2 mixing ratio at each wind direction) times ((hourly CO_2 average mixing ratio at each wind direction) minus (hourly CO_2 average mixing ratio at all the 16 wind directions))**



Spring (CH_4 loading) Summer (CH_4 loading) Autumn (CH_4 loading) Winter (CH_4 loading)

Figure 3: **Atmospheric CH_4 "loading" in spring, summer, autumn and winter at Mt. Waliguan, where loading is defined in Figure 2.**

5.1.2.2 Discrete sampling

As part of the NOAA/ESRL Cooperative Air Sampling Network, discrete air samples are collected in glass flasks approximately weekly at WLG and returned to NOAA/ESRL and the University of Colorado/INSTAAR laboratories in Boulder, Colorado, USA for analysis. Measurements of CO_2, CH_4, CO, H_2, $\delta^{13}C$ and $\delta^{18}O$ of CO_2 started in 1990, N_2O and SF_6 from 1997, and $\delta^{13}C$ of CH_4 from 2002. As of December 2004, more than 660 pairs of air samples were collected and analyzed. Detailed information and data are available at http://www.cmdl.noaa.gov/ccgg/flask.html.

5.1.2.3 Comparison of in-situ measurement and discrete sampling

The WLG continuous in situ and NOAA/ESRL discrete air sample measurements of atmospheric CO_2 mixing ratios at WLG agree (discrete minus continuous, ± 2σ) within 0.59 ± 0.23 ppm for the overlapping monthly means. A comparison of the overlapping discrete and continuous atmospheric CH_4 monthly data records resulted in a mean difference (discrete minus continuous, ± 2σ) of (1.93 ± 2.57) ppb. Figures 4 and 5 shows respectively the comparison results for CO_2 and CH_4 measurement at WLG. The CO_2 and CH_4 data obtained at WLG by the in-situ and discrete measurements has been incorporated into the NOAA/ESRL Cooperative Atmospheric Data Integration Project (CADIP, Globalview-CO_2 2005 and Globalview-CH_4 2005).

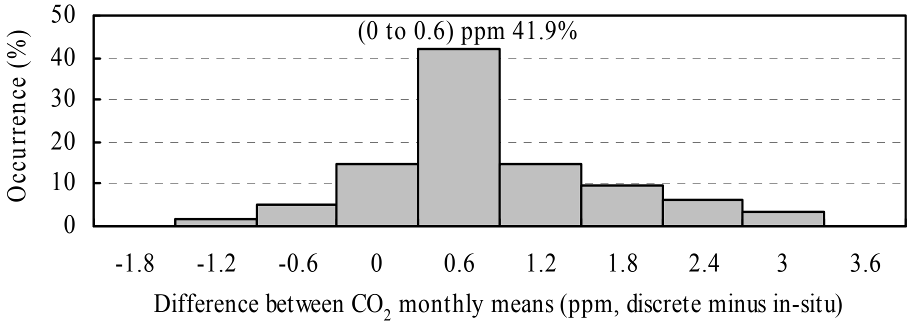


Figure 4: **A comparison of the overlapping monthly mean CO_2 data by the in-situ and NOAA CMDL discrete measurements at WLG.**

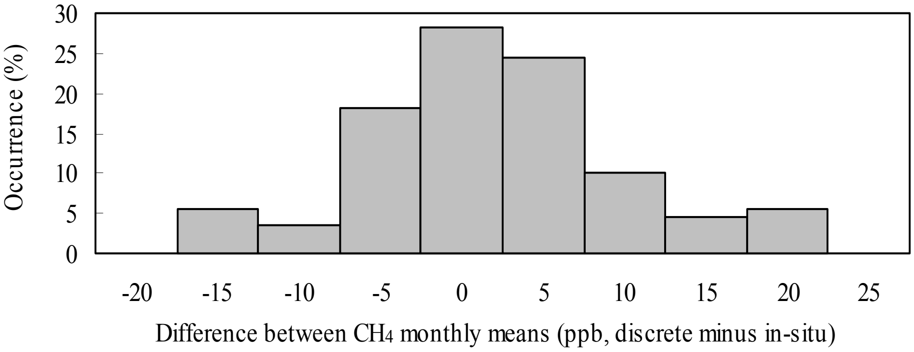


Figure 5: **A comparison of the overlapping monthly mean CH_4 data by the in-situ and NOAA CMDL discrete measurements at WLG.**

5.1.3 Station Standards and Quality Control

Three groups of standard gas tanks (provided by ESRL and MSC, for NDIR, GC-FID and RGA-3, respectively) are used to calibrate the instruments' responses. The CMA (WLG) participated in the WMO round-robin CO_2 inter-comparison organized by the WMO/CCL under NOAA/ESRL, USA for the periods of the 1995-1997 and the 1999-2000 (results available at http://gaw.kishou.go.jp/wcc/co2/comparison.html) as well as the 2002-2005.

The first CH_4 measurement inter-comparison among JMA, KMA, CMA, CSIRO and NIWA was performed in the year 2001-2003 organized by the WMO/WCC under JMA, Japan (results available at http://gaw.kishou.go.jp/wcc/ch4/comparison.html). The second CH_4 inter-comparison among JMA, CMA, KMA and KRISS was started in July 2005. CMA has been finished the measurement at WLG and CAWAS Laboratory in Beijing and sent the CH_4 tanks to Korea.

System and performance audits for surface O_3, CO and CH_4 was conducted at WLG by the WMO World Calibration Centre for Surface Ozone, Carbon Monoxide and Methane (WCC-EMPA) and QA/SAC Switzerland in September 2000 and October 2004, respectively. The official audits reports have been submitted to WMO and distributed to contributors by the WCC-EMPA refer to

EMPA-WCC REPORT 00/3 and WCC-EMPA REPORT 04/3. The results of the 2nd inter-comparisons in 2004 showed good agreement between the WCC-EMPA and the WLG instruments for surface O_3, CO and CH_4. Data quality and data availability at WLG was amongst the best in comparison to other audits conducted at GEF stations by WCC-EMPA. The analysis of the WCC-EMPA transfer standards at the WLG for CO resulted in lower values for the concentrations between 70 and 300 ppb when compared to the WCC-EMPA reference scale. Differences observed between WLG and WCC-EMPA at lower CO concentrations is attributing to uncertainties within the CO scale provided by NOAA/ESRL.

5.1.4 Plans for the Near Future

5.1.4.1 Discrete sampling at the 1+3+3 GAW stations in China

Routine monitoring programme has been extensively enlarged at the three established GAW Regional stations SDZ, LA, LFS since early 2004, following the GAW Measurement Guide and the GAW Strategic Implementation Plan 2001-2007. Moreover, CMA is establishing three new GAW Regional stations ZZ, AKDL and JS with an intensive site investigation and field experiment conducted in 2004-2005. In the near future, discrete air samples will be collected in glass flasks approximately weekly at the 7 GAW stations in China and return to the CAWAS Laboratory in Beijing for analysis of greenhouse gases and related tracers. Currently, the flask preparation line and the integrated laboratory analyzing system are under construction.

5.1.4.2 Intention to establish the GAW QA/SAC China

At the GAW 2005 Workshop in Geneva, CMA announced intention to establish the GAW QA/SAC China and to discuss with other QA/SACs. The structure and responsibilities for the QA/SACs were assumed by various organizations and governments worldwide. With support of the CMA, the Ministry of Science and Technology China (MOST) and a joint effort of the WMO GAW community, the proposed QA/SAC China is going to play a major role in training, quality assurance system, establishing SOPs for GAW measurements, overseeing quality of the data produced under GAW and promoting the use of GAW data especially in China and adjacent regions. Together with atmospheric chemistry observations, research and forecasting programmes in CMA mainly operated by the CAWAS, it will become an essential and promoting part of the GAW and IGACO.

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We would like to thank WLG and other CMA colleagues as well as twining partners from Canada, USA, Australia, Switzerland, Japan and other countries for their kind efforts on the greenhouse gases and related tracers measurements at Mt. Waliguan. We appreciate WMO AREP Environment Division for their intensive coordination on the GAW programme.

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5.2 CO_2 Monitoring and Research Programmes in Hungary

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5.2.1 Monitoring Activities

There used to be two measuring sites in Hungary, K-puszta (46°58'N, 19°33'E, 125 m asl) and Hegyhátsál (46°57'N, 16°39'E, 248 m asl), where the atmospheric mixing ratio of carbon dioxide was continuously monitored. Both stations were located in rural environment, as far as it was possible in the highly industrialized, densely populated Central Europe. At K-puszta, which is the environmental monitoring site of the Hungarian Meteorological Service, CO_2 monitoring was begun in 1981 (*Haszpra*, 1999a). The outdated, worn-out system was shut down in 1999 due to the lack of resources for operation and maintenance.

The monitoring site close to the village called Hegyhátsál is located at a TV transmission station owned by Antenna Hungária Corporation. This greenhouse gas research site is jointly operated by several Hungarian and foreign institutions dominated by the Department of Meteorology, Eötvös Loránd University, Budapest. The ongoing monitoring and research projects receive financial support from the European Union and other funding agencies. Here CO_2 monitoring was started in 1993, in the framework of a U.S.-Hungarian joint research project, in cooperation with NOAA.

The monitoring site called Hegyhátsál is located on a fairly plain plateau in a hilly region in Western Hungary. It is surrounded by agricultural fields (mostly crops and fodder of annually changing types) and forest patches. The small village close to the site has only 170 inhabitants. There is no notable industry in this dominantly agricultural region. The station is fairly free from direct anthropogenic influence.

The base of the measurements is a TV-transmission tower. First a NOAA flask sampling site (station code: HUN) was established here for the global co-operative greenhouse gas monitoring network in 1993. Samples have been taken every week at 96 m above the ground. In late 1994 the continuous monitoring of atmospheric CO_2 mixing ratio was started at four elevations from 10 m to 115 m. Basic meteorological parameters like temperature, humidity and wind are also available from these levels. The system is based on a Li-Cor 6251 analyzer and standards prepared and certified by NOAA. Details of the measuring system are given in *Haszpra* et al. (2001). The data measured are available at WDCGG.

In May, 1997, an ultrasonic anemometer and a fast response Li-Cor 6262 CO_2 analyzer were installed at 82 m above the ground, while in early 1999, in co-operation with NIRE (now NIAIST), Tsukuba, Japan, similar instrumentation was also installed at 3 m elevation. Both systems are used for the continuous determination of the vertical flux of carbon dioxide by means of the eddy covariance technique. The footprint of the measuring system located at 82 m elevation covers several types of ecological systems (agricultural fields of different types, forest patches) while the low level system samples the underlying semi-natural grass (*Haszpra* et al., 2001; *Barcza* et al., 2003; Haszpra et al., 2005). The significant interannual variation in the biosphere/atmosphere exchange of carbon dioxide has inspired us to study the potential environmental factors influencing the process. For this purpose soil temperature, soil water content and radiation sensors have been added to the existing meteorological ones.

In the framework of the EU supported international CarboEurope project the vertical profile measurements of CO_2, CO, CH_4, N_2O, SF_6 mixing ratio, CO_2 stable isotope composition and O_2/N_2 ratio has been extended up to 3000 m above the ground (3250 m above the sea level) over Hegyhátsál by means of regular (one per 3 weeks) airplane measurements. The airplane carries a flask sampler and takes samples at 7 elevation levels (200 m, 500 m, 1000 m, 1500 m, 2000 m, 2500 m, 3000). The samples are analyzed by Laboratoire des Sciences du Climat et de l'Environnnement (LSCE), CEA-CNRS, France, and by the Centrum voor Isotopen Onderzoek (CIO), University of Groningen, the Netherlands.

5.2.2 *Long Term Trend In CO_2 Mixing Ratio*

More than 5 years of reliable parallel data series are available from K-puszta and Hegyhátsál for comparison. At both sites NOAA standards were used for calibration which, in principle, guarantees the comparability. On an annual base the comparison shows little differences (+/-0.5 ppm) during the daytime hours, but remarkable ones during nighttime, especially in summer (*Haszpra*, 1999b). It reflects the differences in the surrounding vegetation, soil composition, and perhaps in climate. That is why it is suggested to take into account only the daytime values in the comparisons, in trend studies in the case of low elevation mid-continental stations. Figure 1 presents the long term trends at K-puszta and Hegyhátsál.

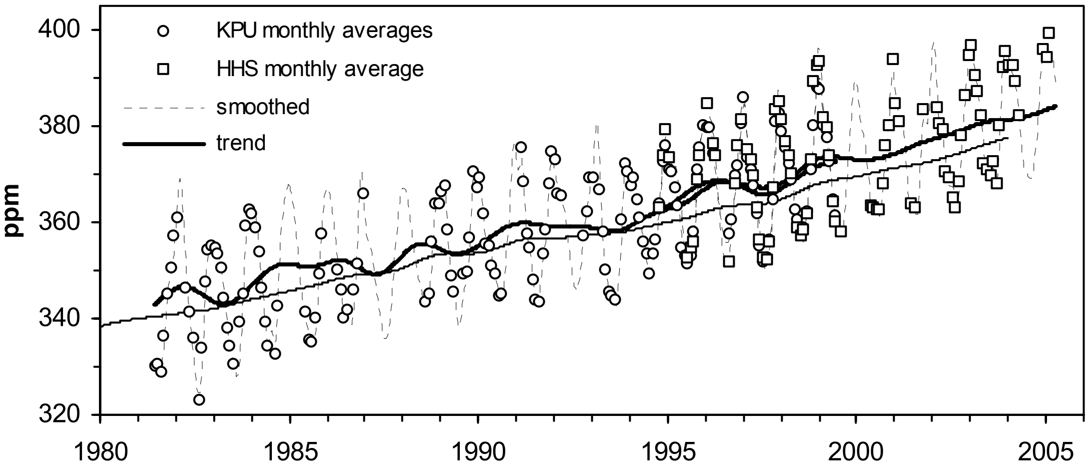

Figure 1: Temporal variations and long term trends of CO_2 mixing ratio at Hegyhátsál (HHS) and K-puszta (KPU) measured early afternoon (12-16 h LST) at 10 m above the ground.

5.2.3 *Short Term Tendencies in the Atmospheric CO_2 Mixing Ratio*

The increasing atmospheric CO_2 concentration enhances the greenhouse effect which may cause global climate change. At the same time the growth rate, seasonal and daily variation of the atmospheric CO_2 concentration are significantly influenced by the activity of the biosphere which is climate dependent. As a consequence, the changes in the shorter term variation in the atmospheric CO_2 concentration may indicate global/regional climate fluctuations.

In the second half of the 90's several papers were published on the increasing amplitude on the seasonal cycle in correspondence with the increasing growing season in the middle and higher north latitudes (e.g. *Chapin* et al., 1996; *Keeling* et al., 1996; *Randerson* et al., 1997; *Zimov* et al., 1999). The Hegyhátsál data record does not show increasing seasonal amplitude. Instead, the amplitude was decreasing especially from the late 90's (Figure 2). The shape of the seasonal cycle was also changing. The start of the "relative CO_2 deficit season" was becoming earlier at an approximate rate of about 1 day/year, while the date of the end of the season remained unchanged (Figure 3). This change and the lower than average trend in the spring mixing ratio (Figure 4) suggest the earlier start of the growing season in the region monitored. However, the higher than average growth rate and the decreasing seasonal amplitude reflect the decreasing summer activity of the vegetation. This idea is also supported by the direct biosphere-atmosphere CO_2 exchange measurements (Figure 5).

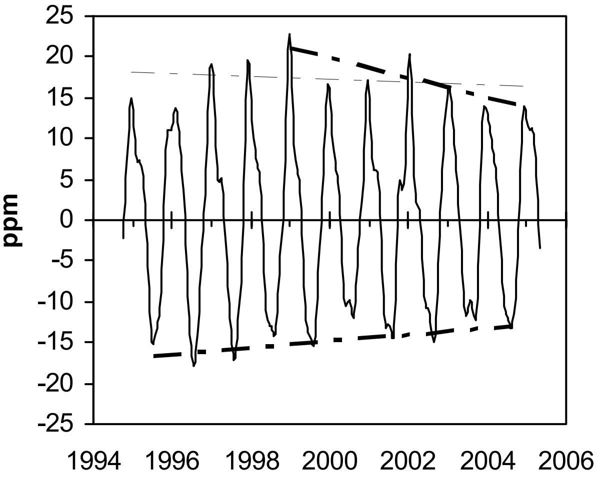

Figure 2: Seasonal variation in the early afternoon (12-16 h LST) CO_2 mixing ratio at Hegyhátsál (10 m above the ground).

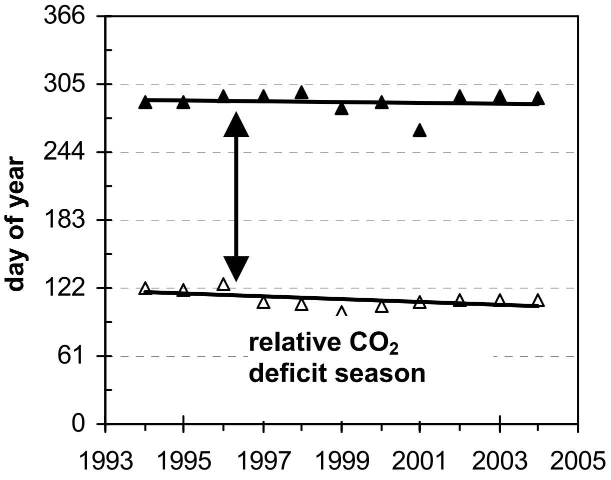

Figure 3: The dates of the sign-change (+ → - and - → +) of the relative CO_2 mixing ratio.

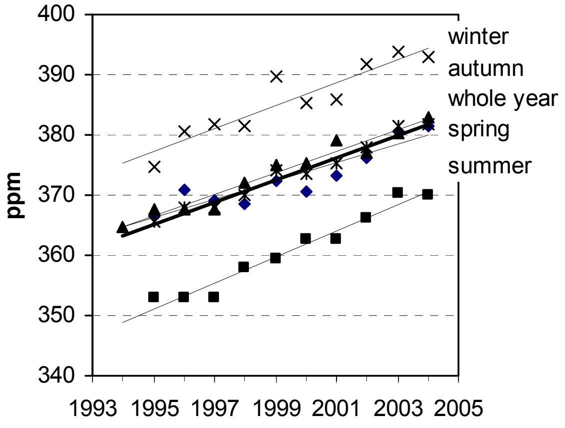

Figure 4: Trends of the seasonal average early afternoon (12-16 h LST) CO_2 mixing ratio at Hegyhátsál (10 m above the ground). Spring - 1.53 ppm/yr, summer - 2.17 ppm/yr, autumn - 1.78 ppm/yr, winter - 1.91 ppm/yr, whole year - 1.85 ppm/yr.

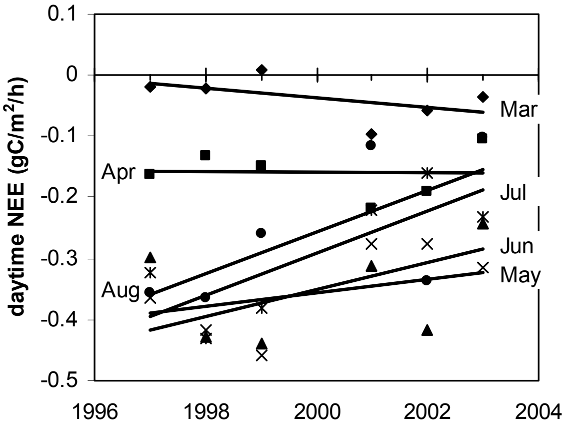

Figure 5: Trends in the daytime (8-16 h LST) net ecosystem exchange (NEE) measured by the eddy covariance system located at 82 m elevation at Hegyhátsál.

Figure 5 shows that the net uptake of the vegetation slightly increased in early spring but significantly decreased in summer, especially in July and August. These changes are the reactions of the ecological systems to the changing environmental conditions, namely to the changing climate. The period from the late 90's until 2003 was warmer and drier than average. Due to the increasingly warm and dry weather (Fig. 6) the vegetation sequestered less and less carbon. While at the beginning of the direct biosphere-atmosphere exchange measurements in 1997 the region of the monitoring site was a moderate net carbon sink, it became balanced by the turn of the century, and by 2003, when the summer was extremely warm and dry, it turned into a remarkable net carbon source. Our measurements prove under natural conditions that the warming climate may turn the biosphere from net carbon sink into a net source.

It seems that the extremely dry and warm period ceased, or at paused, in 2004. The relatively cool and wet weather (which, in fact, corresponded to the long term average - see Figure 6) was favourable for the net biospheric carbon uptake. The ecological systems in the footprint area of the measurements removed approximately 107 g carbon per square meter in 2004, which is comparable with the specific anthropogenic emission (around 175 g C/m^2/yr) of Hungary. The preliminary estimate also indicates a net carbon uptake of a similar magnitude for 2005 when the weather was similar to that in 2004.

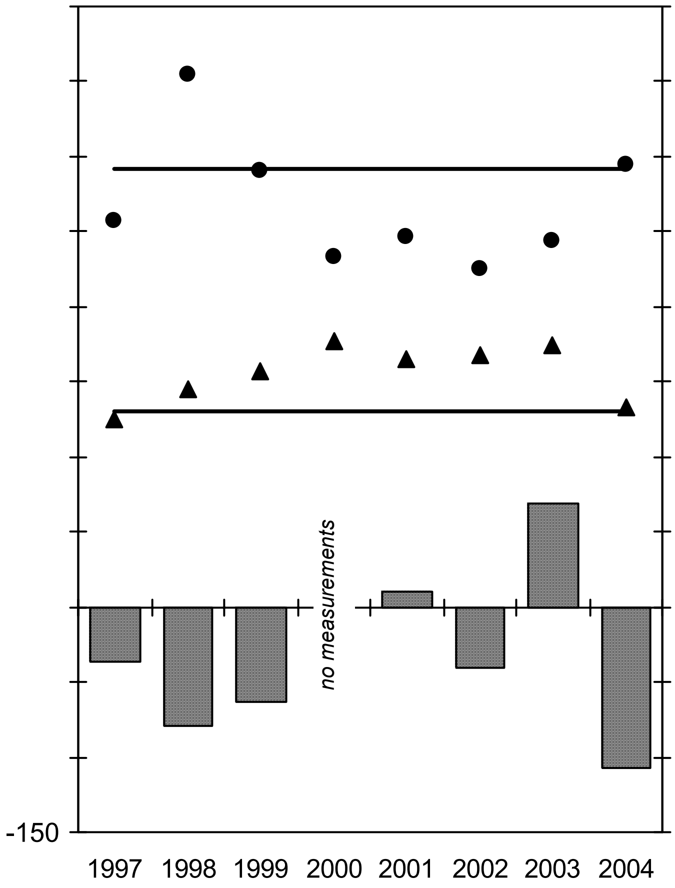

Figure 6: **The net ecosystem exchange (NEE) of the region of Hegyhátsál, as well as the precipitation amount and the mean temperature characteristic for the growing seasons.**

5.2.4 Future Plans

The high precision carbon dioxide vertical profile measurements, as well as the direct vertical CO_2 flux measurements at 3 m (to be resumed in 2006) and 82 m above the ground will be continued. The measuring system will be completed by GC based quasi-continuous methane, nitrous oxide, sulfur hexafluoride and carbon monoxide measurements. The regular aircraft flask sampling will be continued and it will be completed by high frequency (once per 5 days) CO_2 profiling from 2006. The almost unique length of the NEE record allows us to adapt and/or develop a process oriented ecosystem model for the prediction of the future carbon budget of the region. A sophisticated footprint model is also under development for the better interpretation of the mixing ratio and flux measurements.

Acknowledgments

Use of the TV-tower and transmitter building is kindly provided by Antenna Hungária Corporation. The research projects were/are supported by the Hungarian National Scientific Research Fund (T32440 [2001-2004] and T42941 [2003-2006]), by the European Union 5th and 6th R&D Framework Programmes (AEROCARB - EVK2-CT-1999-00013 [2000-2003], CHIOTTO EVK2-CT-2002-00163 [2003-2006], CarboEurope-IP, contract no. GOCE-CT-2003-505572 [2004-2008]), and by the Hungarian Ministry for Economy and Transportation (GVOP-3.2.1.-2004-04-0107/3.0 [2005]). The trend lines and the fitted smoothed functions in Figure 1 were calculated by means of the software developed and described by *Thoning* et al. (1989).

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5.3 India's Initiatives in Greenhouse Gases Monitoring

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5.3.1 Introduction

Detection of an anthropogenic climate change signal in observed climate data, as reported by the recent Scientific Assessment of the Intergovernmental Panel on Climate Change (IPCC 2001), lays credence to the validity of climate change predictions through model simulations. The prime responsibility of the scientific community now lies in elimination of the uncertainties that still remain with these predictions. As a first measure, we need to improve our evaluation of the radiative forcing agents that are primarily responsible for climate change. Atmospheric composition of the radiatively active species viz. Greenhouse Gases (GHGs) and aerosols, and their trends need to be accurately determined with adequate spatial coverage to improve estimates of radiative forcing. Observational data on GHGs and aerosols are lacking from South and South-east Asia. The knowledge of carbon fluxes in these regions, involving some of the greenhouse species directly and many of them indirectly, are also lacking.

An inventory of anthropogenic emissions of GHGs in India has been prepared under National Communications *(NACOM)* (Figure 1). The assessment of GHGs inventory that identifies and quantifies a country's primary anthropogenic sources and sinks of GHGs is central to any climate change study. India has prepared its national communication as per Revised 1996 IPCC Guidelines for National Greenhouse Gas Inventories covering all major GHGs including carbon dioxide (CO_2) methane (CH_4) and nitrous oxide (N_2O) (NATCOM 2004). The contribution from CO_2, CH_4 and N_2O emissions were 65 percent, 31 percent and 4 per cent of total GHGs emissions in 1994, respectively. However, on sectoral basis, 61 percent of CO_2 equivalent of GHGs were emitted from energy sector, 28 percent from agriculture, 8 percent from industrial processes, 2 percent from water disposable and 1 percent from land use, land use changes and forestry (LULUCF) sector.

The national CO_2 emissions from all energy, industrial processes and LULUCF activities constituted 65 per cent of the total GHG emissions in 1994. The relative contributions of the three activities to the net CO_2 released from India were 85 per cent, 13 per cent and 2 per cent, respectively. CH_4 emissions in 1994 from agriculture sector dominated with 78 percent followed by 16 percent from the energy systems and 6 percent from waste disposal activities. Similarly, the agricultural sector accounted for 85 percent of total N_2O, while contributions from fuel combustion, industrial processes, waste and biomass burning accounted for 6 percent, 5 percent and 4 percent in 1994, respectively.

However, there is no systematic programme to evaluate natural emissions and sinks of GHGs and the existing levels of their concentrations. Accurate data of emissions and sinks are essential for carbon cycle modelling, addressing climate change issues and prioritizing mitigative measures.

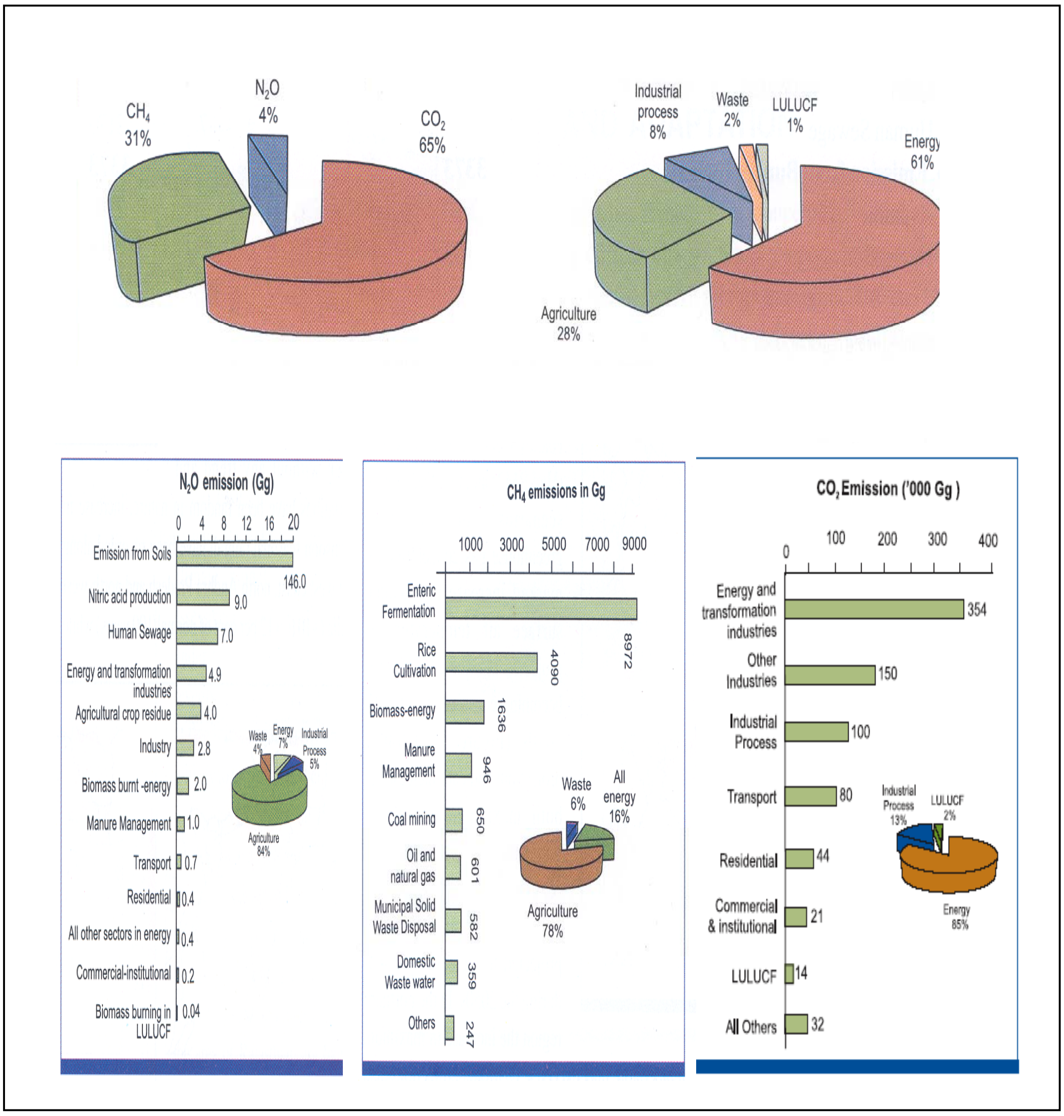

Figure 1: **Emission of Greenhouse gases in India (NATCOM 2004).**

5.3.2 New Initiatives

5.3.2.1 Climate Related Environment Monitoring (CREM)

A dedicated monitoring network is required to capture seasonal and long term trends in various climate and physio-graphic regions of India (Figure 2). A multi-agency programme named CREM for monitoring greenhouse gases and aerosols has been initiated to address above shortcomings in present state of knowledge in the Indian sub-continent with following objectives:

- To establish and operate a permanent network of stations in India to monitor the atmospheric composition of radiatively active species (CO_2, CH_4, N_2O, O_3 & *Aerosols*).
- To establish a GHG reference laboratory and national GHG standards linked to international standards.
- To establish a CREM data centre and engage in capacity building in relevant areas.

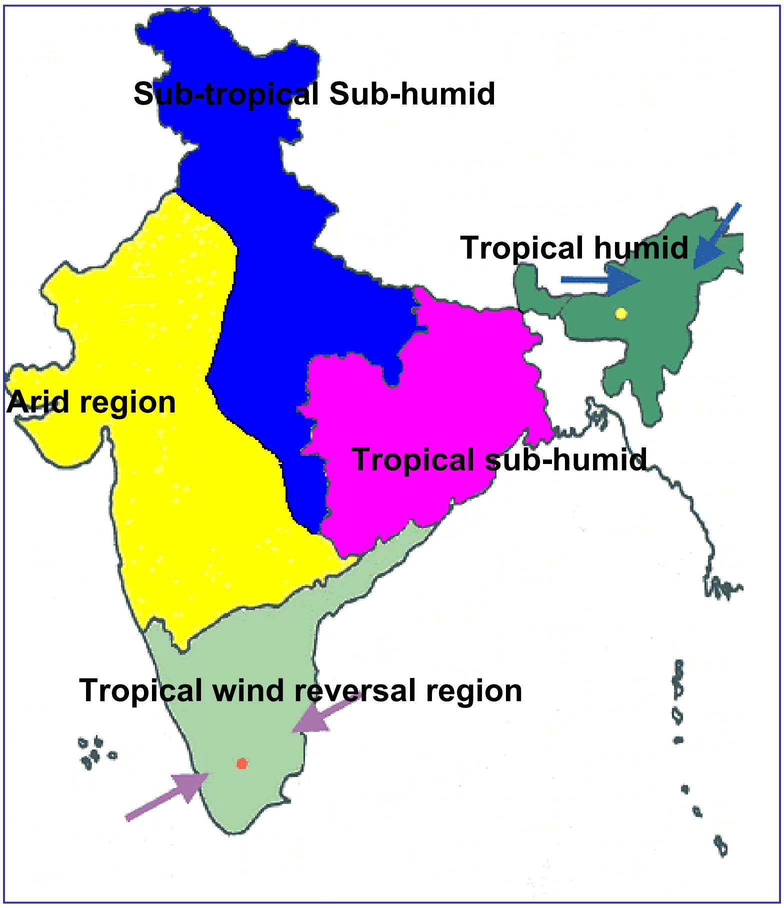

Figure 2: **Physio-graphic and climatic regions of India.**

5.3.2.1.1 Components of CREM

The CREM programme has been divided into the following 10 separate projects covering all the parameters of interest.

- GHG Ambient air, Continuous *insitu* monitoring (CO_2, CH_4 *and* N_2O).
- GHG Ambient air, Discreet *grab sample* monitoring (CO_2, CH_4 *and* N_2O).
- GHG emission flux, *insitu* measurements (CH_4 *and* N_2O).
- GHG Reference Laboratory and National Standards.
- Column CO_2 measurements.
- Ozone monitoring programme (Surface, Total Column & Vertical profile- O_3).
- Precursors of Ozone.
- Aerosols characterization.
- Aerosol - radiative flux measurements.
- CREM Data Centre and Capacity Building.

5.3.2.1.2 Monitoring strategy

Online GHGs Measurements

Online GHG measurements (CO_2, N_2O, and CH_4) will be made by analyzers located at the station (*in situ)* using an NDIR technique which are capable of yielding continuous data and more accurate estimate of long-term mean values and their trends. The baseline monitoring in the Indian subcontinent is to determine the carbon sequestering capacity of our evergreen forests and vegetated regions and their underlying soils. On top of this, there is a modulating influence of inter-hemispheric exchange of air masses in the monsoon regions. Representative baseline sites in northern and southern India have been selected where international protocols will be followed to monitor GHGs and inter-comparision experiments will be carried out. Details of monitoring sites and data/ sample exchange are presented in Figure 3.

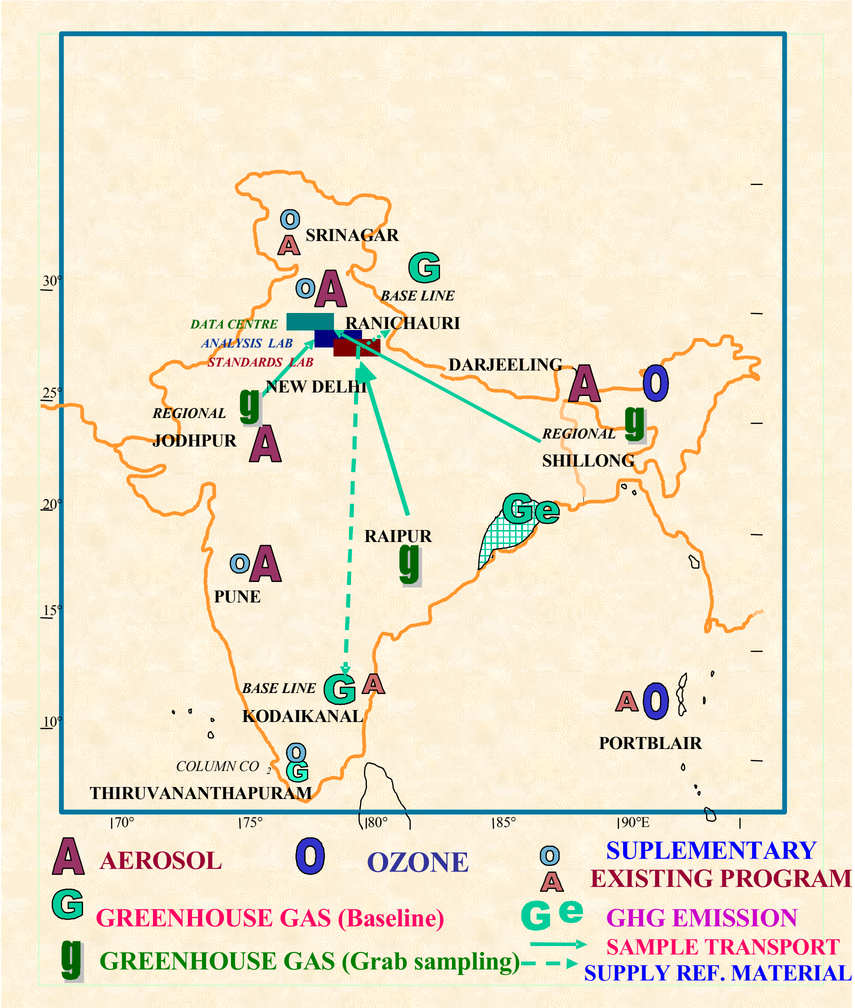

Figure 3: **CREM Network.**

Grab Sampling Programme

A supporting programme with an off line grab sampling strategy is being implemented to capture regional impacts. The thrust would be on seasonality of the variations. This programme will target forest areas of northeast India, the dwindling forest region of Central India and a desert location in the west chosen as a control experiment site, against which the variability of forested regions would be compared.

Soil organic matter and large volumes of organic litter are generated in different regions over the Indian sub-continent. Further, organic compounds and mineral nutrients in water bodies control the fluxes of various gases. There is a pressing need to estimate residence time of CH_4, N_2O *and* O_3 in the atmosphere so as to determine their long-term impacts.

GHGs Emission Flux Programme

Emission of GHGs from un-aerated soils (wetlands and inundated conditions) is another important objective of study. There is a proposal in CREM to directly measure such fluxes (in contrast to measurement of ambient concentrations) from wetland areas of Orissa. The emission rates will be characterized by other environmental factors of the soils and waters, *viz*. nutritional status, microbial status, *etc.* to generalize the data with respect to causative indicators.

Reference Standards

The Reference Material laboratory will be set up in Delhi to calibrate the field measurements against international standards translated to National GHG standards. Such a programme is necessary for comparing data globally and use in global carbon cycle modelling.

Ozone Measurements

Vertical O_3 profiles are highly variable in time and space. Thus, vertical O_3 profiles in typical areas representative of urban, rural, maritime and biomass burning regions need to be monitored. As a standard practice vertical profiles need to be normalized against the Total Column Ozone content, which in turn will be measured by sun-photometric techniques like the Brewer Spectrometer and the portable sun-photometers.

In addition to being a GHG, O_3 is chemically reactive and affects the carbon cycle in a significant way through oxidation of CH_4, organic compounds etc. Major sources of ozone are in the stratosphere and lower troposphere. Study of Ozone chemistry at the surface is essential to assess the rate of formation and destruction in lower regions.

Aerosols

The aerosol programme will be run from Shillong (North-east India). This location has a mixture of carbonaceous aerosols from local and sub-regional sources and sulphate aerosols from distant continental sources in East Asia, transported with the trade wind regime. Measurements would also be conducted in north-west India (Delhi) representing a mixture of mineral and urban aerosols. Both locations have a mixture of aerosols with significantly different radiative properties.

Aerosol populations need to be characterized by their size distribution at surface and in vertical and by their chemical composition at surface to identify local sources. It is also important to know the real and imaginary components of the refractive index of bulk column aerosols, which can be determined by using a Sky Radiometer.

CREM Data Centre and Capacity Building

The Indian Meteorological Department will be the nodal centre for archival of all data sets which will be generated by CREM. The CREM Data will be put in the public domain *via* the Internet for a pre-decided set of parameters. Exchange of raw data and other relevant information will be allowed among the concerned parties.

7.3.2.2 Flux programme

A new initiative has emerged in India to directly measure vertical fluxes of gases in the Boundary Layer over various biologically active regions of the country. The ultimate aim of this exercise is to refine the Global Carbon Cycle model by using the gridded inventory of regional fluxes and confirming the ambient concentrations from the baseline data of the Indian region.

5.3.3 Acknowledgements

The author is thankful to Sh. B. Lal, Director General of Meteorology and Sh. Sanjiv Nair, Permanent Representative of India with WMO for kind permission to participate in above meetings and WMO for extending financial support.

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5.4 CO_2 Measurements at the Sites of the Italian Observing Network

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5.4.1 Introduction

Atmospheric carbon dioxide is continuously monitored at three different sites in Italy: the two mountain stations at Plateau Rosa and Monte Cimone and the marine station in the island of Lampedusa. The stations are operated by three different institutions: the Italian Electrical Experimental Centre (CESI), the Italian Air Force Meteorological Service and ENEA respectively. Through a partnership among these institutions a programme for comparing the measurements from the existing sites has been created. In this report a short comparative analysis of the three time series will be presented. A description of the measurement methods was given in a previous report (WMO, 2005).

5.4.2 Observational Sites

Plateau Rosa station is located in the North-East Italian Alps (7.70° E, 45.93 °N, 3480 m a.s.l.) facing Mt. Cervino. This is one of the highest atmospheric monitoring stations in the world. The station is located on a plateau nearby a glacier on its north-eastern side and a sharp rocky slope on the west. During summer some vegetation grows on the southern slope nearly 1000 m below. Around the site, for several kilometres, there is no significant human influence on the measurements except during winter, due to tourist activity. On a larger scale, the Po Valley to the South, and the Rhine valley to the North, with their persistent anthropogenic sources can affect the CO_2 measurements. Continuous measurements were started in 1993.

The second station is located on the top of Mt. Cimone (44°11'N, 10°42'E, 2165m a.s.l.), the highest mountain of the Northern Italian Apennines. The peak is rocky and covered only by some patches of grass. The maximum elevation at which trees grow is about 500 metres below the station level and snow covers a large amount of the surrounding area for 6-7 months per year. Around the site, for several kilometres, there is no significant influence from human activities. The Po Valley, with its persistent anthropogenic source, lies about 60 km to the north at sea level. Mt. Cimone is the windiest meteorological station in Italy, the prevailing winds blow from SSW and NNE. CO_2 has been continuously monitored here since 1979.

A third station is operational on the island of Lampedusa (35.5°N, 12.6°E, 45m a.s.l.). The island has an area of about 20 km^2 with relatively few inhabitants, is rocky and has sparse vegetation. Lampedusa lies in the central Mediterranean sea, about 100 km east of Tunisia and 200 km North of Libya. Prevailing winds blow from NNW. Weekly flask sampling was started at Lampedusa in 1992. Continuous CO_2 measurements were started in 1998. The positions of the three sites are shown in Figure 1 and the wind roses in Figure 2.

5.4.3 Diurnal Cycle

The average amplitude for the diurnal cycle as a function of month in a typical year is shown for each of the three stations in Figure 3. A rather large amplitude can be observed at Mt. Cimone during summer months. This is due to air lifting from the surrounding valleys and reaching the top of the mountain during daytime hours. During the remaining months the site is usually above the planetary boundary layer and the amplitude of the diurnal cycle is very small. At Plateau Rosa, summer amplitudes are lower than that of Monte Cimone thanks to the higher elevation. The flat diurnal cycle of Lampedusa is typical of a marine boundary layer station.

Figure 1: Atmospheric CO_2 measurement site locations.

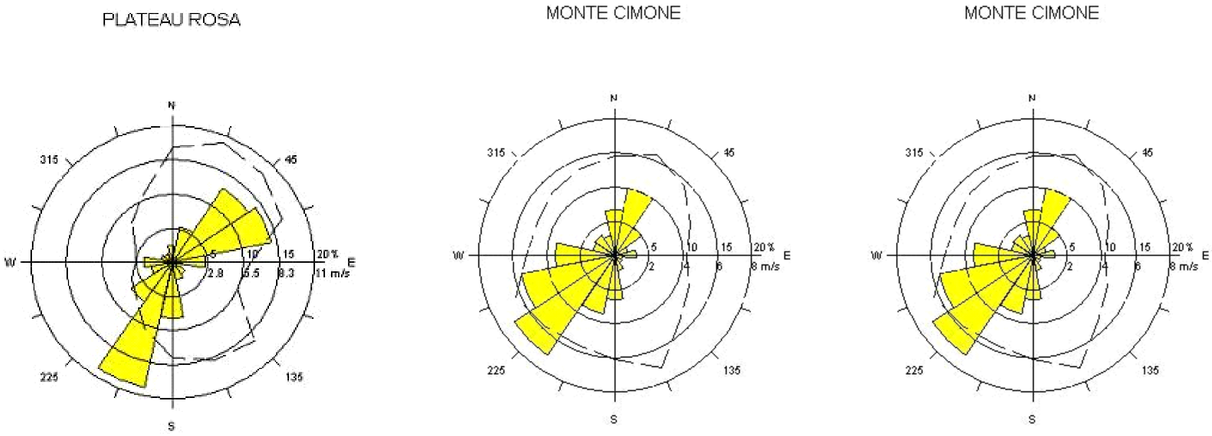


Figure 2: Wind roses for Plateau Rosa (a), Mt. Cimone (b) and Lampedusa (c).

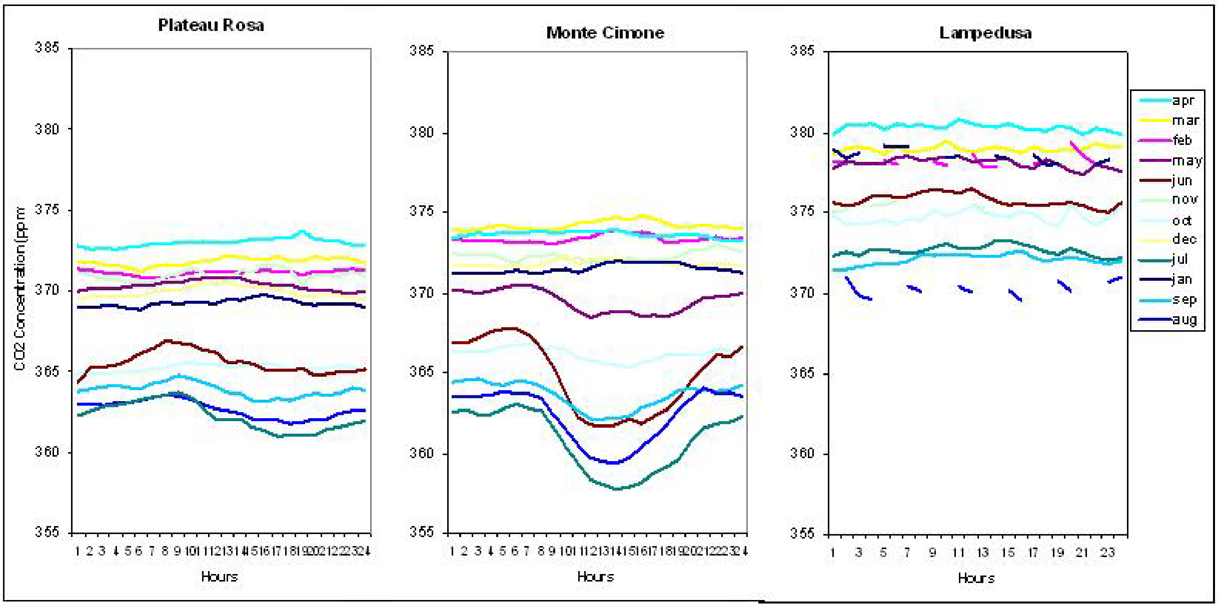


Figure 3: Diurnal cycles in a typical year (2002) for Plateau Rosa (a), Mt. Cimone (b) and Lampedusa (c).

5.4.4 Data Selection

Due to the different characteristics of the sites each station uses a different procedure to select data unaffected by local scale processes.

5.4.4.1 Plateau Rosa

The Procedure is based on the NOAA/ESRL scheme and is summarized as follows:

- Evaluation of the monthly mean and standard deviation.
- Test 1: data with a difference between two consecutive half hourly values <0.3 ppm are accepted.
- Test 2: the absolute value of the difference between each value and the monthly mean must be less than the monthly standard deviation.
- New evaluation of monthly mean and standard deviation.
- Loop until the standard deviation is < 1 ppm.
- New evaluation of unselected values.
- Test 3: absolute value of the difference between each value and the monthly mean < 3 ppm and standard deviation <1.2 ppm.

5.4.4.2 Monte Cimone

The procedure routinely used to select hourly means unaffected by local processes is based on Thoning *et al.* (1989) and is summarised in the following lines.

- Visual inspection of the raw data.
- Hourly means with standard deviation greater than a cutoff value are discarded.
- Hourly means with a difference with respect to the previous hour greater than a preset value are discarded.
- Summer data between 9am and 9pm are temporarily discarded.
- A cubic spline curve passing through the daily means is created.
- An iterative routine discards data too far from the resulting curve.

The procedure has been recently modified and improved. Results are under study.

5.4.4.3 Lampedusa

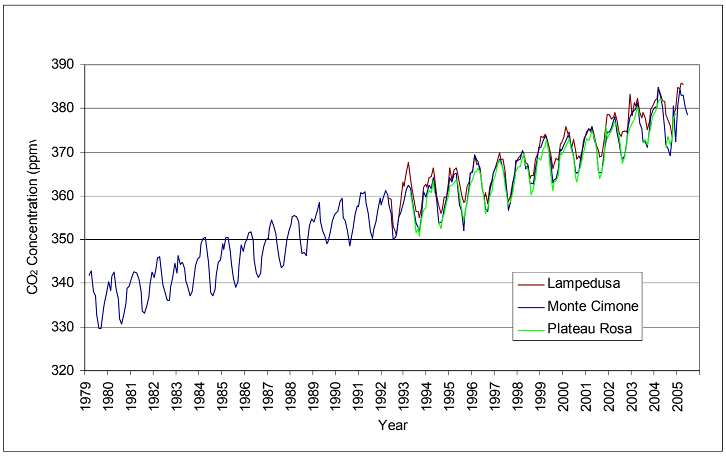
The identification of the background CO_2 concentration is based on the following steps:

- Elimination of measurements potentially contaminated by local pollution by removing cases that correspond to specific wind sectors.
- Elimination of data displaying standard deviation of the CO_2 hourly average > 0.5 ppm.

Additional analyses based on air mass trajectories are under investigation.

5.4.5 Time Series Analysis

The monthly means of the selected data are shown for the three stations in Figure 4. Winter measurements at Mt. Cimone are generally larger than that of Plateau Rosa, while at Lampedusa the concentrations recorded in summer are smaller than that of the two mountain stations. Causes of the differences in the seasonal component among the stations are under study. The growth rates of the trends are shown for the three stations together with the Southern Oscillation Index in Figure 5. The curves seem well correlated. A common positive peak is evident on June/July 1998 occurring with a lag of about 7 months after an intense El Nino event. In 2001/2003 another common positive peak can be observed, not related to any El Nino event. It is also worth noting the minimum in the growth rate at Monte Cimone on January 1992, seven months after the eruption of Mt. Pinatubo and the maximum in 1983 7 months after another El Nino event.



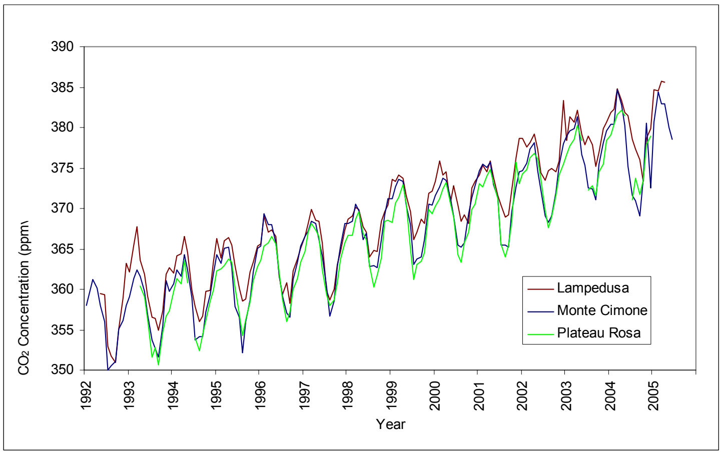


Figure 4: Comparison of the monthly averages of CO_2 concentrations measured at Plateau Rosa, Mt. Cimone and Lampedusa for the periods 1979-2004 (top) and, for better comparison, 1992-2004 (bottom).

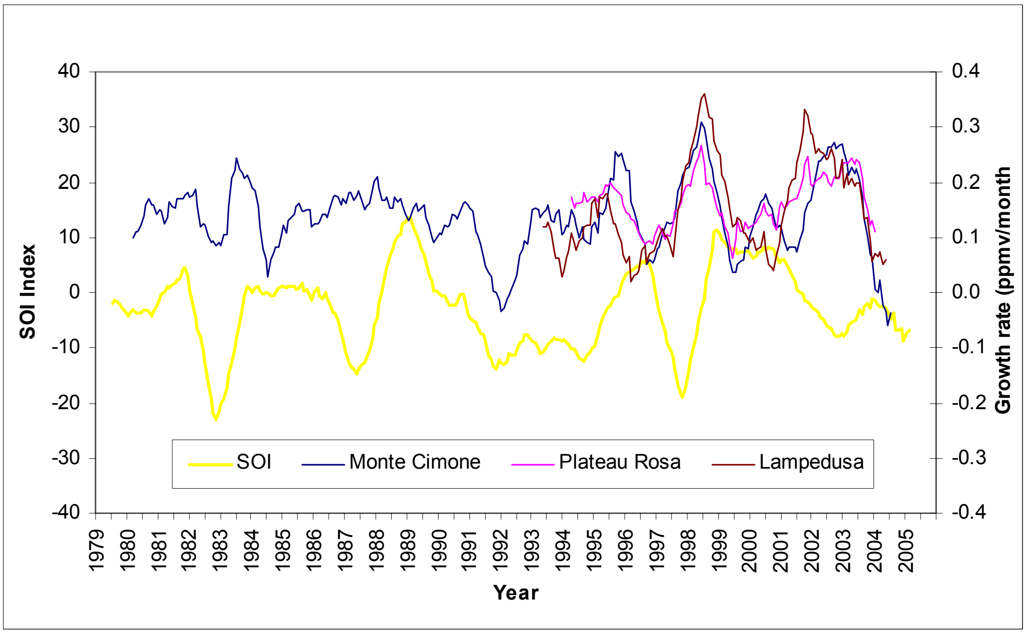


Figure 5: Growth rates of the CO_2 mixing ratios in comparison with the SOI.

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5.5 Developments in the Pallas GAW Station Activities

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5.5.1 Introduction

Pallas GAW station, in northern Finland, has been undergoing major changes in recent years. The main site, Sammaltunturi, was rebuilt in 2001 and since then the number of components measured have increased considerably. Two new sites, Kenttärova (micrometeorological CO_2 flux measurements above a spruce forest) and Lompolojänkkä (CO_2 and CH_4 flux measurements in wetland) were built and began operation in 2002 and 2005, respectively. In addition the area has two other sites, Matorova (filter and wet deposition sample collection) and Laukukero (automatic weather station), see the map in Figure 1. More detailed description of the sites and overview of the results, except for Lompolojänkkä, can be found in Hatakka et.al., (2003).

The Finnish GAW station Pallas-Sodankylä has another node at Sodankylä where, for example, upper-air and spectral radiation measurements are routinely conducted. Sodankylä has also a micrometeorological flux site above a Scots pine forest. These three flux sites cover the three most common land-use classes in Finnish Lapland providing CO_2 source and sink estimates of natural surfaces.

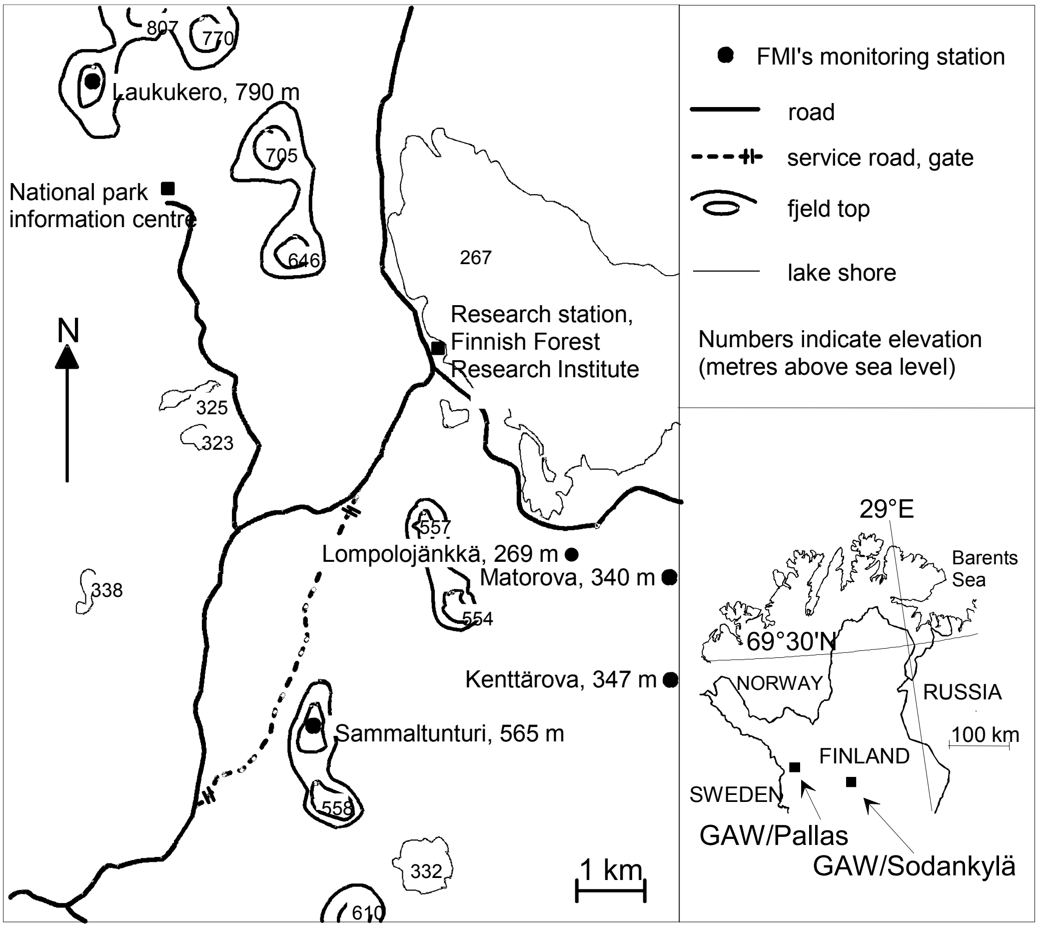

Figure 1: **Locations of FMI's measuring stations at Pallas.**

5.5.2 Sammaltunturi

Sammaltunturi is the main site at Pallas measuring continuously ozone, SO_2, NO_x, CO_2, CO, CH_4, N_2O, SF_6, aerosol size distribution, scattering, absorption and number concentrations, radon, and different meteorological parameters. In addition samples are collected twice weekly for volatile organic compound analysis, and since 2002 also NOAA cooperative sampling network flasks have been collected weekly.

In spring 2004 a new system was installed for measuring CH_4, CO, N_2O and SF_6. Instrument is based on a GC with FID and µECD detectors with external interface and a custom made programme. Carbon monoxide is measured with FID after converting it to methane with a nickel catalyst. Sample and working standard (dried natural air) are measured alternately. One measurement takes 7.5 minutes, i.e. 4 atmospheric and working standard samples are measured in an hour. Working standards are calibrated against 3 CH_4/CO, and 5 N_2O/SF_6 standards from NOAA a few times a year.

Back trajectories are calculated routinely for the station, 8 trajectories a day with 120 hour length. These trajectories have been used to classify transport of carbon dioxide to the station (Eneroth et al., 2005).

5.5.3 Kenttärova

Kenttärova lies on a hill top plateau ca. 60 m above the surrounding plains. A 20 m high measurement tower is situated in a Norway spruce forest aged between 70 and 170 years. At the station CO_2 and sensible and latent heat fluxes are measured using eddy covariance technique at the height of 23 m (Aurela et al, 2001, Aurela et al., 2005). The high-frequency (10 Hz) instruments used for flux measurements are Metek USA-1 sonic anemometer together with LiCor-7000 CO_2/H_2O analyzer. Fluxes are calculated as 30 min average covariances by custom built software, which makes the standard flow rotation and non-ideal high-frequency corrections. Calibrated CO_2 concentrations are measured at three different heights (gradient), and during summer respiration chamber measurements are also conducted at the site. In addition, the station has an extensive set of meteorological measurements including temperature and humidity profiles in air and soil, global and reflected solar radiation, long-wave radiation upwards and downwards, photosynthetic photon flux density (PPFD), net radiation, snow cover depth and cloud layer height.

An example of CO_2 fluxes and concentrations, together with some meteorological data is given in Figure 2. During this midsummer period CO_2 uptake by the ecosystems were at their highest and strong diurnal cycles of fluxes were observed. The CO_2 fluxes are downwards (negative) during the day when there is net uptake by the forest from the atmosphere. At night, when photosynthesis is low, soil and plant respiration dominates and the net flux is upwards (positive). In summer the maximum net uptake in full daylight conditions is around 0.4 mg CO_2 m^{-2} s^{-1} at Kenttärova and at Sodankylä about half of that (0.2 mg CO_2 m^{-2} s^{-1}). Lower uptake rates at Sodankylä are due to rather low green biomass amount of the Scots pines (projected Leaf Area Index 1.2) compared to the spruce forest (LAI 2.2). From mid-June to mid-July the CO_2 uptake increases at the spruce forest but the pine forest has already in mid-June full uptake capacity. At Sammaltunturi, a generally decreasing CO_2 concentration trend is observed due to uptake by vegetation in the northern hemisphere. Superimposed on that seasonal trend are diurnal concentration variations. The concentration increases during late night and early morning hours, drops sharply in the morning and often declines gradually during the day. These variations are a result of net respiration and development of stable boundary layer at night, formation of a convective boundary layer in the morning and CO_2 net uptake and growth of the boundary layer during the day. In the beginning of July, temperatures were very high, above 25 °C. At that time CO_2 uptake was depressed, probably due to high temperatures and low humidity, and CO_2 concentration variations were low.

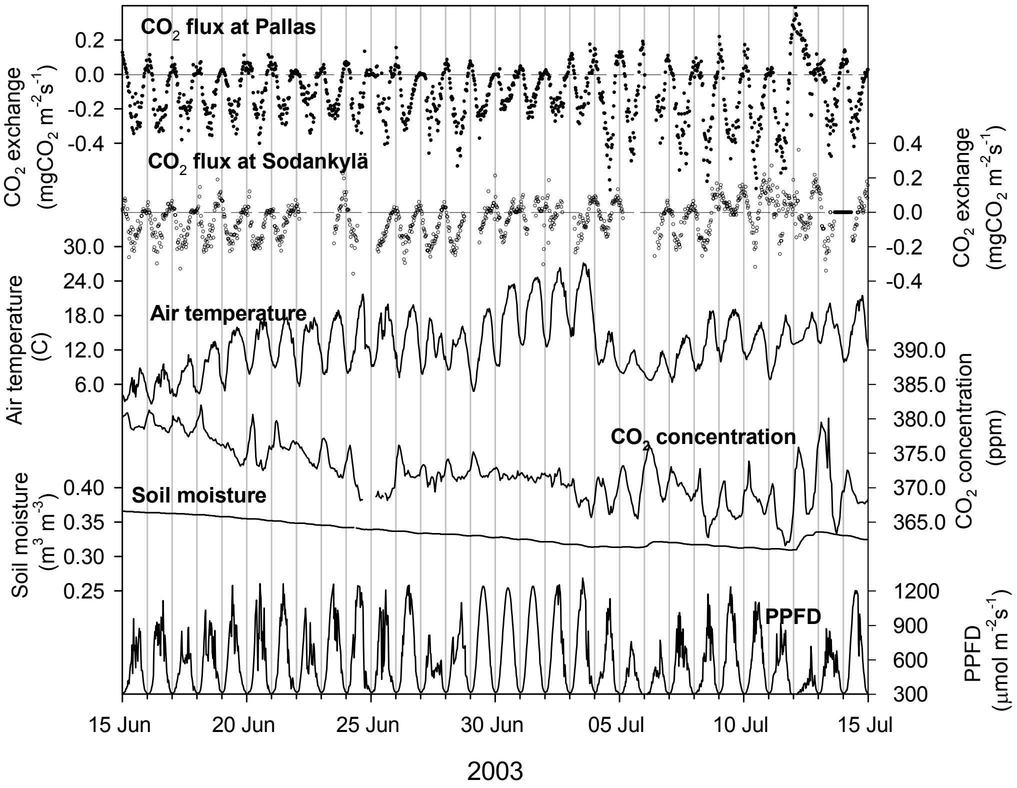

Figure 2: **CO_2 fluxes at Kenttärova spruce forest (Pallas) and at Sodankylä Scots pine forest from 15 June to 15 July 2003. Air temperature (2 m), soil volumetric moisture (-10 cm) and PPFD are measured at Kenttärova. The background CO_2 concentration is from the Sammaltunturi station.**

5.5.4 Lompolojänkkä

Lompolojänkkä is a subarctic aapa mire (wetland). These aapa mires have a typical noontime net uptake rates of about 0.25 mg CO_2 m^{-2} s^{-1} in midsummer (Aurela et al., 2001), and they are significant sources of methane to the atmosphere. In northern Finland summertime methane emission rates on the order of 500 ng m^{-2} s^{-1} have been observed. Lompolojänkkä site was established to quantify the local source because of observed elevated CH_4 concentrations at Sammaltunturi. These high concentrations are particularly clear in some summer nights.

Measurements at the station include CO_2 and CH_4 fluxes with eddy covariance technique, and CO_2 and CH_4 concentrations at two heights. The CO_2 flux measurement system at Lompolojänkkä is similar to that at Kenttärova, except for the measurement height, 2.5 m. For CH_4 fluxes, a FID is used as a fast response sensor to measure total hydrocarbon flux (Laurila et al., 2005) by pumping the air directly to the FID through a pressure controller to stabilize the flow. We assume that the total hydrocarbon flux is a good estimate of the methane flux. Calibrated CH_4 concentrations are measured chromatographically by another FID in the same GC. This system uses one column, has two minute cycle length and uses one working standard of dried natural air.

Methane concentrations at Sammaltunturi vary between 1825 and 1900 ppb, the smallest concentrations being found towards the summer, reflecting general seasonal trend (Fig. 3). During calm nights, when stable atmospheric stratification restricts vertical mixing, hourly mean concentrations may be up to 450 ppb higher at the wetland site. The concentration difference is much smaller, up to 26 ppb, in daytime when the boundary layer is well-mixed. The gradient increases towards the midsummer due to the accelerated production of methane in the warming inundated peat layer, and because the developing sedge vegetation acts as a transport conduit of the gas.

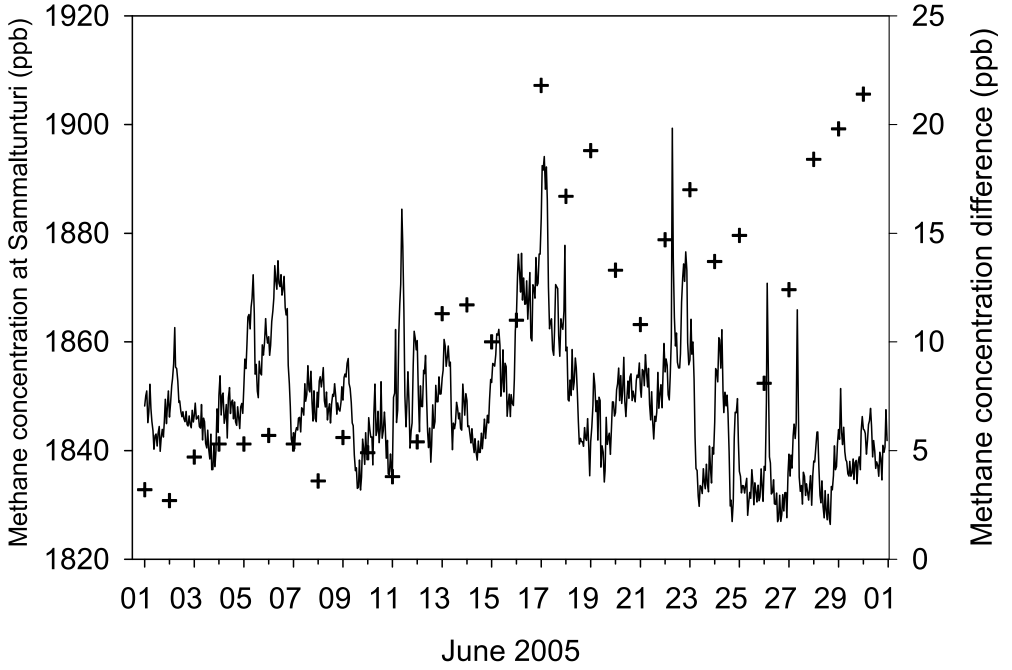

Figure 3: **Methane concentration in June 2005 at Sammaltunturi (left axis) and concentration difference (+ symbols) between Lompolojänkkä and Sammaltunturi at 12:00 – 16:00 non-DST local time.**

5.5.5 Conclusions

The flux and concentration measurements at the forest and wetland sites, 200-300 m below the hilltop site, help us to quantify the effect of surrounding vegetation and changing weather on the concentrations at the GAW main site. Concentration and flow field in the area have been simulated using a fluid dynamics model to further understand modifications of the concentrations at the GAW site by the local terrain and natural sources (Aalto et al., 2005). Further developments at Pallas include starting of continuous hydrogen concentration measurements during 2006 at Sammaltunturi.

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5.6 RAMCES: The French Network of Atmospheric Greenhouse Gas Monitoring

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5.6.1 Introduction

The RAMCES CO_2 and Radon-222 monitoring programme was initiated in 1980 at the Amsterdam Island observatory [Gaudry et al., 1983; 1990; Monfray et al., 1996; Ramonet et al., 1996] and was extended at Mace Head, Ireland, in 1992 [Bousquet et al., 1996; Biraud et al., 2000; 2002] and at two further sites in France (Saclay and Puy de Dome, 2001). The three western European sites reflect different environments from a marine site occasionally influenced by long range transport over Europe (Mace Head), to sites which are more influenced by rural (Puy de Dôme) and urban activities (Saclay). Continuous measurements of CO_2 and Radon-222 have been established in each observatory and CH_4, N_2O, SF_6 and CO are measured at Saclay. In addition, a flask sampling programme was initiated at LSCE in 1996. Flasks are sampled at 12 fixed surface sites, three on-board small aircrafts and ships in Indian Ocean and North Atlantic. At LSCE, the samples are analyzed for CO_2 isotopes ($\delta^{13}C$ and $\delta^{18}O$) and for CO_2, CH_4, N_2O, SF_6 and CO mixing ratios. In this report we will describe our existing network and the plans of extension during the next years. A further focus is on the tests of the Loflo CO_2 analyzer performed and the description of the flask analysis facility.

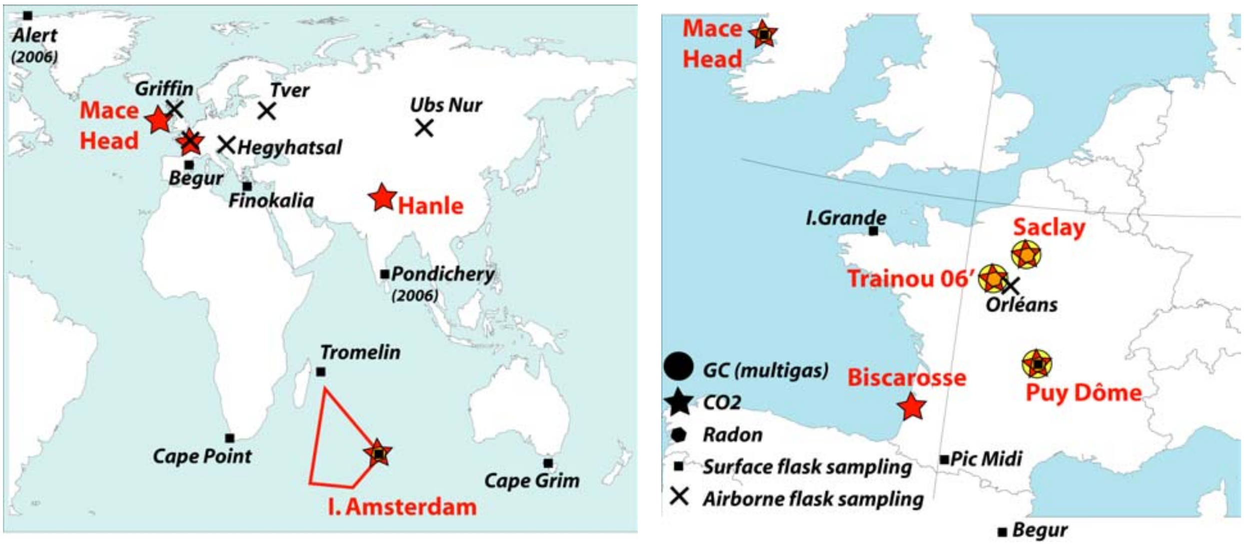

Figure 1: **RAMCES flask sampling and in-situ measurement network. The different symbols represent the instrumentation and the type of sampling, and the red polygon in the right-hand figure refers to a shipboard sampling track.**

5.6.2 Continuous CO_2 Measurements

Figure 2 shows daily average CO_2 mixing ratios at our four established measurement sites: Amsterdam Island, Mace Head, Puy de Dome and Saclay. In 2005 we added two new stations Biscarosse (France) and Hanle (India) to our network, which are both equipped with a newly developed CO_2 analyzer (CARIBOU). More details on the instruments and stations (Table 1) are given by Galdemard *et al.* in this issue. In 2006 we will equip a new site in Orleans Forest, France (Trainou Tower) with a GC system and a CARIBOU in order to analyze in-situ CO_2, CH_4, N_2O, SF_6 and CO at 3 heights (50m, 110m and 180m). In the future, Orleans will be a "supersite" for RAMCES with multiple species being measured at the tower and vertical profiles from aircraft up to 3000m. Our airborne programme at the forest of Orleans was initiated in 1996 with flask sampling between 100 and 3000m with a frequency of two to three flights per month. Within the European project CARBOEUROPE we were installing an insitu CO_2 analyzer (Condor) in the small aircraft and increasing the frequency to 2 flights per week. During the next two years we will upgrade Puy de Dôme station with a gas chromatographic system and install a CARIBOU CO_2 analyzer at Mace Head.

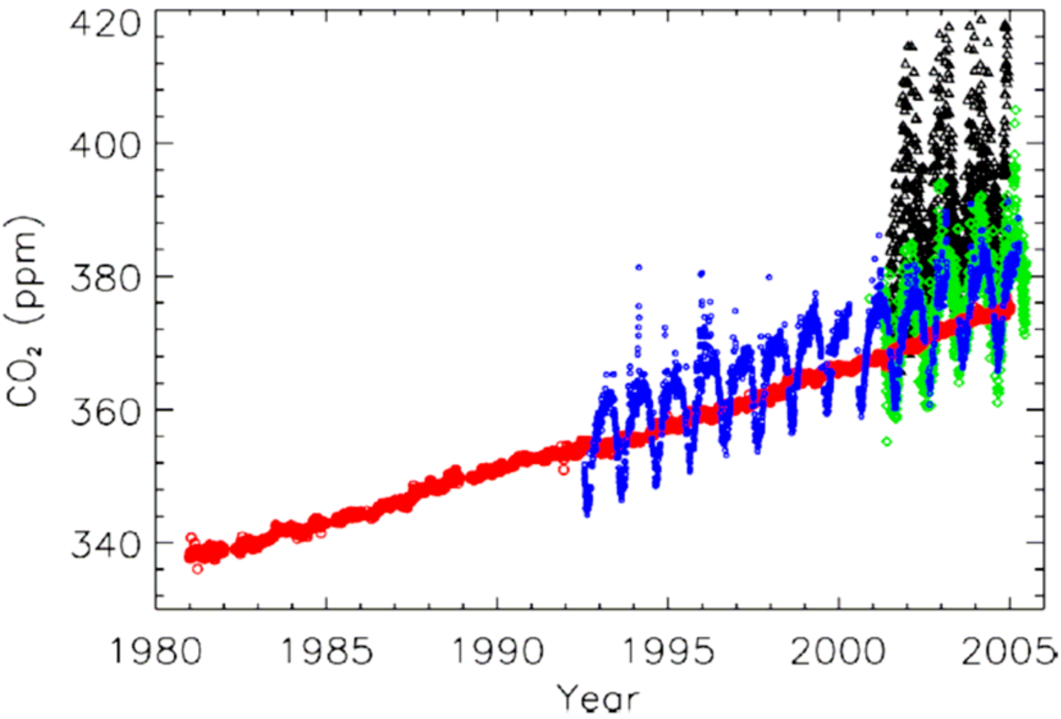

Figure 2: **CO_2 mixing ratios at Amsterdam Island (red), Mace Head (blue), Puy de Dôme (green) and Saclay (black).**

Table 1A: **In-situ measurement sites of RAMCES.**

Site	ID	Country	Latitude	Longitude	Alt. (m asl)	Species	Instrument	Période
Ile Amsterdam	**AMS**	France	37°57'S	77°32'E	70	CO_2 CO_2 Rn222 Météo	URAS/Siemens LOFLO CAFAR/Dérouleur	1980-… 2006-… 1967-…
Mace Head	**MHD**	Ireland	53°20'N	09°54'W	25	CO_2 Rn222 Météo	Siemens Dérouleur	1992-… 1996-…
Puy de Dôme	**PUY**	France	45°45'N	03°00'E	1465	CO_2	Licor	2001-…
Gif-sur Yvette	**GIF**	France	48°43'N	02°09'E	20	CO_2 CO_2 CO_2, CH_4, N_2O, SF6 CO Rn222 Météo	LOFLO CARIBOU Multi-GC GC-CO Dérouleur	2005-… 2006-… 2001-… 2004-… 2001-…
Biscarosse	**BIS**	France	44°22'N	01°'13'W	120	CO_2	CARIBOU	2005-…
Hanle	**HLE**	India	32°46'N	78°57'E	4517	CO_2	CARIBOU	2005-…
Trainou (Orleans Tower)	**TRA**	France	47°58'N	2°07'W	390	CO_2 CH_4, N_2O, SF6, CO Rn222 Météo	CARIBOU Multi-GC ANSTO	2006-…

Table 1B: **Flask measurement sites of RAMCES.**

Site	Latitude	Longitude	Alt. (m)		Start	Interval	Collaborator
Ile Amsterdam	37°57'S	77°32'E	70	France	1996	4 / month	IPEV
Mace Head	53°20'N	9°54'W	25	Ireland	1996	4 / month	UGC
Puy de Dôme	45°45'N	3°00'E	1465	France	2001	4 / month	LaMP
Orléans [1]	48°50'N	2°30'E	100-3000	France	1996	2-3 / month	Météo France
Tver [1]	56°28'N	32°55'E	100-3000	Russia	1998	1 / month	BGC, IPEE
Hegyatsal [1]	46°57'N	16°39'E	100-3000	Hangary	2001	2 / month	HMS
Griffin [1]	56°36'N	3°47'W	100-3000	Scottland	2001	2 / month	IERM
Ile Grande	48°35'N	4°40'W	20	France	1998	2 / month	-
Tromelin	15°53' S	54°31'E	20	France	1998	4 / month	Météo France
Cape Grim	40°41'S	144°41'E	94	Austalia	1998	2 / month	CSIRO
Begur	41°58'N	3°13'E	13	Spain	2000	4 / month	U. Barcelona
Finokalia	35°19'N	25°04'E	130	Greece	2001	2 / month	U. Heraklin
Hanle	32°46'N	78°57'E	4517	India	2000	3 / month	IIAP
Pic du Midi	42°56'N	0°08'E	2877	France	2001	4 / month	LA - OMP
Marion Dufres [2]	Indian Ocean		20		1996	2 / year	LBCM

5.6.2.1 Test of the high precision CO_2 analyzer (Loflo)

In 2003 we purchased two high precision CO_2 analyzers (LoFlo) from CSIRO-AR. One LoFlo was installed in January 2004 at LSCE to serve as our reference instrument to propagate the NOAA-WMO scale to all the secondary standard gases used in the observatories. The second LOFLO was installed at our station in Amsterdam Island. During the last 18 months we tested the LOFLO installed in our lab intensively. The CSIRO LoFlo Mark2 CO_2 analyzer is an integrated system constructed around a LI-COR 6251 (Non Dispersive Infrared (NDIR) analyzer). The LoFlo system maintains ultra-high precision using solid state flow and pressure controller of the LI-COR gas flow, coupled with careful attention to the selection, testing and treatment of all surfaces fittings that interacts with the gas composition. The current LoFlo setup permits three basic modes of operation (see Figure 3):

- CALIBRATION (CAL). Determines the Reference Cylinder CO_2 concentration, and LI-COR response (linearity), relative to up to 7 calibration cylinders containing dry air with independently assigned CO_2 concentration.
- MONITOR (MON). Uses the response function and assigned reference cylinder concentration from a prior calibration to determine the CO_2 concentration in dried ambient air.
- TANK (TNK). Uses the response function and assigned reference cylinder concentration from a prior calibration to determine the CO_2 concentration in up to five pressurized containers of dry air.

During our test at LSCE we were using mostly CAL and TNK mode. Our instrument is connected to a set of 7 calibration cylinders filled at CSIRO and calibrated by WMO-CO_2 CCL at NOAA/ESRL in Boulder, USA. These cylinders span a CO_2 range between 320 and 460 ppm. During calibrations at LSCE the 7 cylinders are measured starting at the lowest CO_2 concentration cylinder and stepping through each cylinder to the highest concentration and back to the lowest (pyramid). Continuous measurement persists for 10 minutes on each cylinder, bracketed by 10 minutes of measuring the reference cylinder. A full calibration (18 pyramids) takes 3.5 days of measurement with a gas consumption of only 5.5l per cylinder. The calibration assigns a best fit quadratic curve to describe the LI-COR response and assigns a CO_2 concentration to the reference cylinder, for use in subsequent measurements in MON and TNK modes. Figure 4 shows the variation of three reference cylinders between January 2004 and May 2005. The reference gases show an extremely constant behaviour with a standard deviation of only 0.003 or 0.001 ppm until end of August. In September we moved the complete LoFlo analyzer with calibration cylinders in a different laboratory. This short disturbance (several hours, were the pressure regulators were not connected to the calibration cylinders) resulted in a significant higher value (0.04 ppm) for the reference cylinder during the following two calibrations. After three weeks, the system was again fully operational with the high precision obtained before.

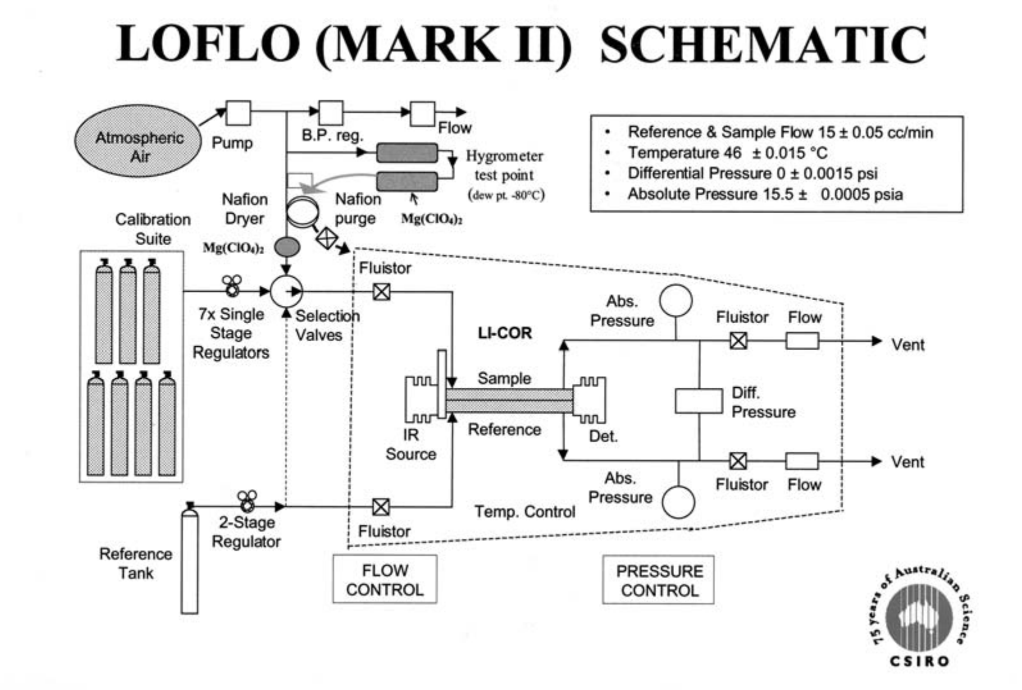

Figure 3: **Schematic of the Loflo CO_2 analyzer.**

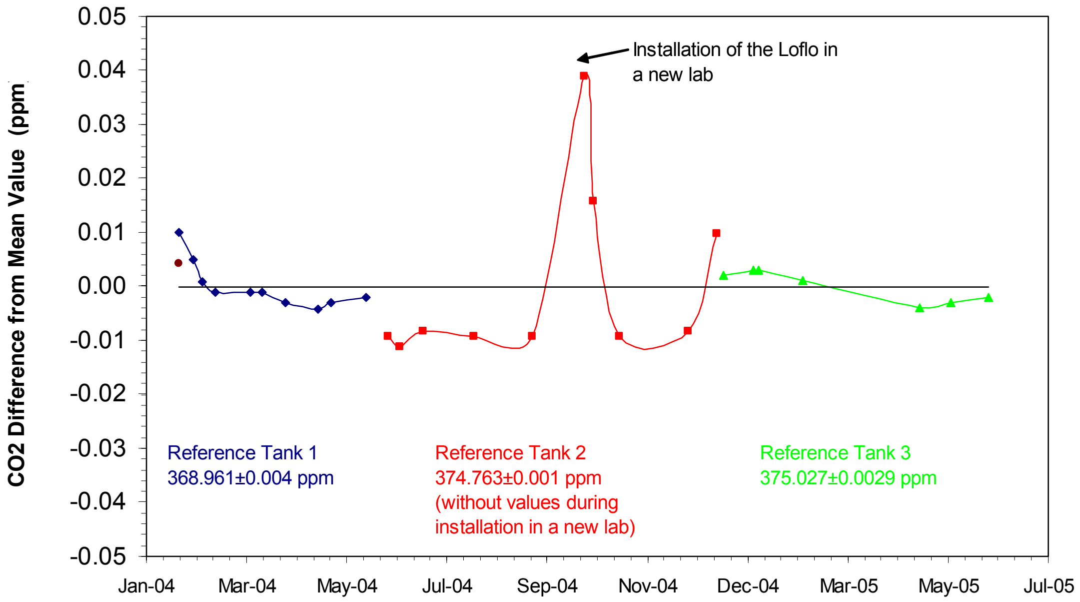

Figure 4: **Variation of three Loflo reference gases between January2004 and May 2005.**

The LoFlo analyzer shows a stability of the span which is not comparable to instruments which were used before. A calibration of the span was traditionally performed every 2-4 hours, whereas the recommendation for the LoFlo was every 2 month. Figure 5 shows the difference from the real value, when using the calibration performed on Oct-15 instead of the calibrations performed regularly for a concentration range of 341 to 434 ppm. For a concentration close to the reference cylinder the difference is, with the exception of the period right after moving the instrument, in the range of only 0.01 ppm. For higher concentrations (434 ppm) we can clearly see a drift of the span during 6 months. Therefore we conclude that for marine stations like Amsterdam Island a calibration every two month will be sufficient, whereas for analyzing tanks (using the full range) one calibration per month is needed for a precision better than 0.05 ppm (WMO recommendation for Southern hemisphere).

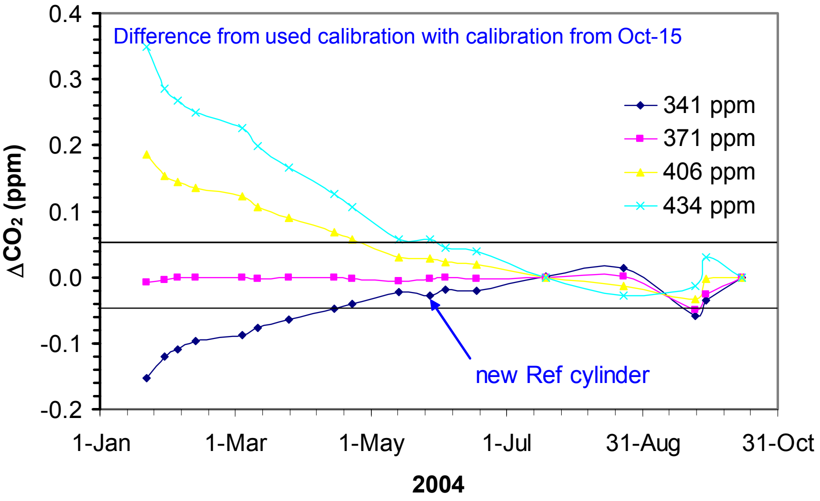

Figure 5: **Difference from the used calibration to the calibration performed on Oct-15 for a CO_2 concentration range between 341 and 434 ppm. Gray lines show calibration differences of ±0.05 ppm.**

For our tests with the Loflo we used two sets of calibration cylinders:

1. A set of 9 CO_2 calibration tanks, filled and analyzed at the WMO-CO_2 CCL (NOAA/ESRL) in Boulder, USA.
2. A set of 7 tanks filled by CSIRO-AR (Melbourne, Australia), with clean southern hemispheric air, analyzed at the WMO-CO_2 CCL (NOAA/ESRL) in Boulder, USA in 2002.

With these 2 sets of tanks, we are in the unique position to assess the influence of more polluted North Hemispheric air on our high-precision CO_2 measurement instrument (LOFLO). This is a further step to improve the measurements.

The set of 7 cylinders filled by CSIRO-AR are connected permanently to the Loflo, whereas 7 tanks filled by NOAA/ESRL were analyzed as “unknown” samples.

Table 2: **Comparison of 8 high pressure cylinders analyzed at NOAA/ESRL and with the LoFlo at LSCE.**

	NOAA/ESRL			LOFLO			LoFlo - NOAA
Cylinder	n	CO_2 (ppm)	σ	n	CO_2 (ppm)	σ	CO_2 (ppm)
CA05384	3	353.307	0.006	6	353.204	0.006	-0.102
CA05396	3	368.977	0.040	3	368.916	0.006	-0.061
CA05399	3	400.760	0.010	3	400.760	0.005	0.000
CA05347	3	411.94	0.053	3	411.965	0.003	0.025
CA05392	3	432.327	0.045	3	432.304	0.012	-0.013
CA05372	4	448.755	0.093	3	448.740	0.002	-0.015
CA05346	3	480.337	0.047	6	480.048	0.019	-0.270

Table 2 summarizes the comparison of our LoFlo measurements with NOAA/ESRL performed on 7 high pressure cylinders. In the concentration range of 400 to 450 ppm we found very good agreement of both measurements whereas the cylinder CA05384 (353 ppm)showed a difference of 0.1 ppm. To investigate this difference, we will continue to analyze high pressure cylinders in both laboratories. In contrast, the large difference observed for cylinder CA05346 is due to the non-linear behavior of the NDIR analyzer and the calibration range of the LoFlo, which ends at 460 ppm.

In addition we performed a comparison of the LoFlo with our gas chromatographic system, which is used to analyze flasks, and found agreement within 0.05 ppm for high pressure cylinders filled from natural air. The LoFlo was used as well to analyze more than 20 low pressure cylinders ("melons") to monitor the stability of these containers as part of the TACOS-Infrastructure European programme.

5.6.3 Flask Sampling Network And Measurement Facility

As an extension of the RAMCES monitoring network, a flask sampling programme was initiated at LSCE in 1996. Flasks are sampled in fixed surface sites, on-board small aircrafts [*Ramonet et al., 2002*], and ships in Indian Ocean and North Atlantic (Figure 1). At LSCE the samples are analyzed for CO_2 isotopes ($\delta^{13}C$ and $\delta^{18}O$) and for CO_2, CH_4, N_2O, SF_6 and CO mixing ratios.

5.6.3.1 CO_2, CH_4, N_2O and SF_6 analysis of flasks samples

Since September 2000, an automated gas chromatographic system (HP-6890) developed by Doug Worthy (Atmospheric Environment Service, Environment Canada [Worhty et al., 1998]) and optimized at LSCE for measurements of CO_2, CH_4, N_2O and SF_6 in flask samples as well as for semi-continuous measurements of ambient air in Gif-sur-Yvette has been operational This system is equipped with two detectors to analyze simultaneously CH_4 and CO_2 on a flame ionization detector (FID) and N_2O and SF_6 on an electron capture detector (ECD). We coupled a second GC with FID (HP-6890) in order to analyze CO on the same sample (Pepin et al, 2003, Valant et al., 2005). A sample is injected every 5 minutes. We are using two calibration gases, which are injected every 30 minutes. These working standards are analyzed against a set of 3 standards calibrated by NOAA/ESRL. As quality control we are injecting a "target gas" from a cylinder every 2 hours. On average we are analyzing about 2200 flasks per year including samples, test flasks and quality control flasks.

Since 2003 we introduced "flask targets" as additional quality control. Flasks were weekly filled from a known high pressure cylinder. One of these flasks is analyzed within each sequence where flask samples are measured. Figure 6 shows the time series of the flask target for CO_2, CH_4, N_2O and SF_6 since 2003. The standard deviation shows for most species a slightly higher variation than our reproducibility due to uncertainties during flask filling.

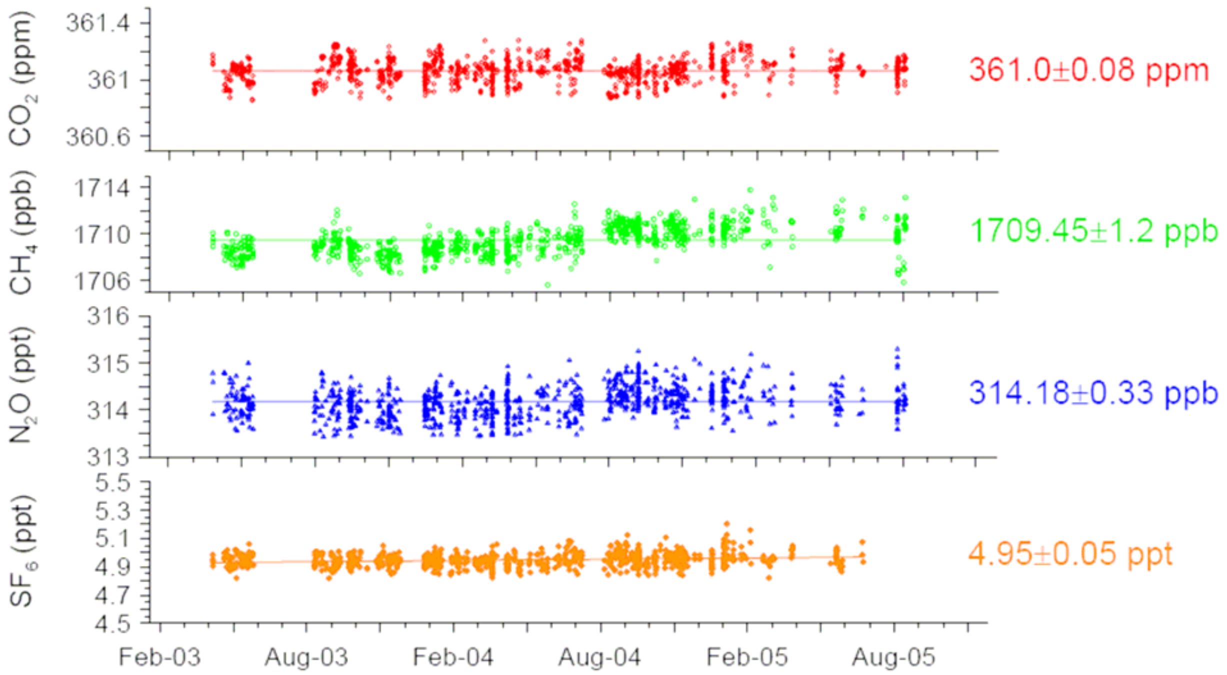

Figure 6: **Time series of "flask targets". Flasks are filled from a high pressure cylinder and one of these flasks is analyzed with each sequence as quality control.**

5.6.3.2 Analysis of CO$_2$ isotopes

Isotopic measurements of atmospheric CO$_2$ (δ^{13}C and δ^{18}O) began at LSCE in 1994-1995 and have been developed since that time. Measurements are made on a Finnigan MAT 252 mass spectrometer. Preliminary analyses were made on pure CO$_2$ gas standards and on air test samples using a manual extraction method. Later on, an automated multi-port device was designed and adapted at LSCE to trap the CO$_2$ in air. It was based on a modified automatic trapping box system from Finnigan and consisted on two cold traps followed by a third micro-volume trap used to re-condensed the CO$_2$ after the initial trapping [*Bourg and Ciais*, 1998]. Isotopic analyses were conducted as follows: the sample and pure CO$_2$ standard gas (Turc αinternal LSCE standard) were introduced in the mass spectrometer change-over valve and measured alternatively 8 times. At the end of each measurement, interfering masses were determined by peak jumping and used for corrections. The Turc LSCE standard was derived from another pure CO$_2$ working standard prepared from purified fossil carbonate and industrial CO$_2$. Both mixtures were then calibrated against international standards (V-PDB, NBS 19 and NBS 20). Since then all the isotopic measurements conducted at LSCE have been obtained using this procedure. Quality control of the air measurement and of the method was checked using two complementary standard air cylinders (Bleu and Noir, initially provided and calibrated by Scripps) used alternatively during each measurement sequence.

Due to increasing maintenance requirements and an increasing number of samples to be analyzed within the RAMCES network, we recently designed a new trapping system following three main goals: get a reliable, simple and precise device. In cooperation with Willi Brandt from MPI Jena we set up of a trapping box similar to the one working at BGC-Jena and described in detail in [*Werner et al.*, 2001]. This new design enables us to analyze 13 sample flasks and 5 standards gas in about 14 hours and to run sequences during nights. The new system was set up in mid February 2005 and tested during the following three months. Routine measurements were restarted in mid-May 2005, following a new experimental protocol and ensuring better quality control on the measurements. The measurements are still conducted by comparison against the Turc α but the final calculations are made using our "bleu" air standard as an air reference gas. Each sequence of measurement now begins with two analyses of the bleu standard, then six samples, then the other air standard “noir” followed by seven samples, and finally ends with two new bleu measurements. The final isotopic values are then calculated against the “bleu” and corrected for CO_2 and N_2O. The measurement of noir acts as a “target gas” and ensures the validity of the sequence. Figure 7 focuses on the stability and reliability of the bleu and noir standard since the set up of the new trapping box. The results exhibit no significant drifts in the measurements of the two cylinders and a quite good reproducibility. Looking in more details to the time series, and applying a raw filter to the data (excluding data values with deviation larger than ±0.05 ‰ from the “true value”) shows that less than 10% of all the data are rejected and more than 80% of those values can be excluded for experimental reasons (at the beginning of the measurements we encountered some trouble with pressure adjustment of one of the below of our mass spectrometer and also we also encountered some contamination problems with our tanks pressure regulators. Both problems have then been fixed and the results over the 2006 are less noisy than at the beginning (see Figure 7).

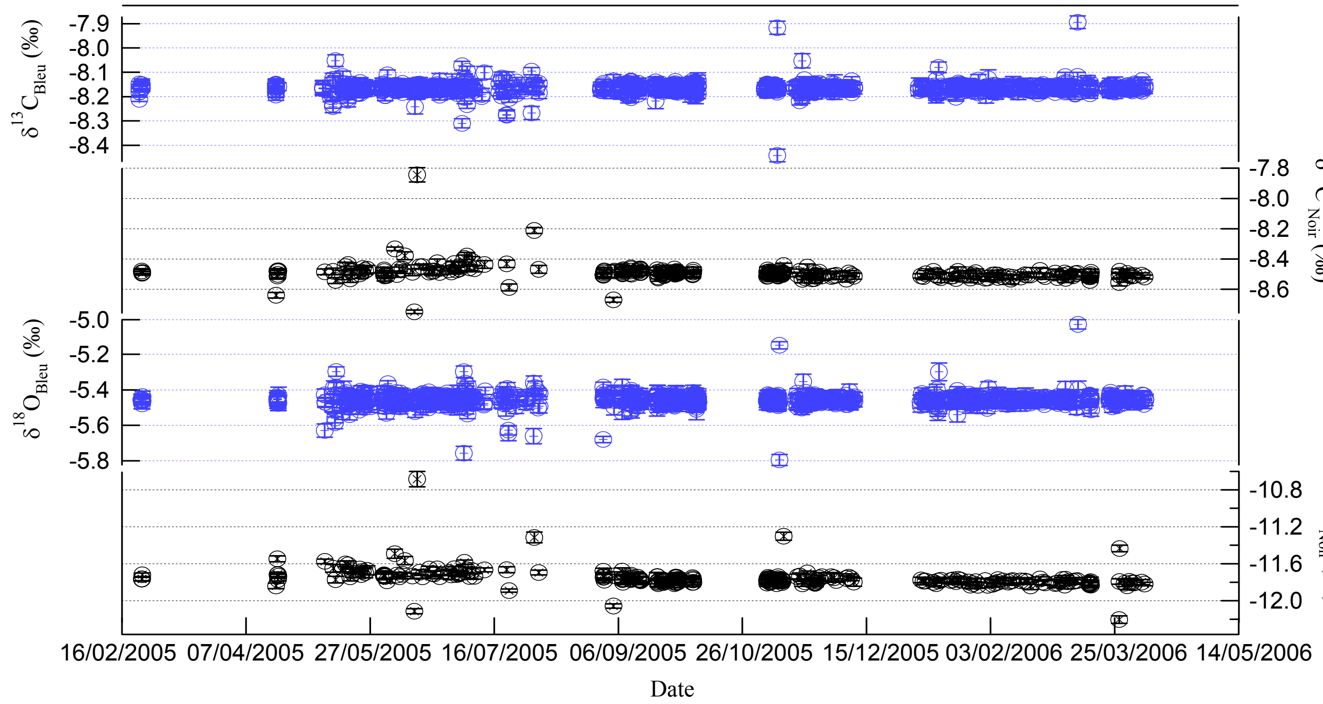

Figure 7: **Measurement of two ambient air cylinders (blue and noir) with the new trapping box.**

In addition to this target gas measurement, we systematically use target flasks filled with air with a well know isotopic signature. These day-to-day quality control procedures are reinforced by regular inter-comparisons with other laboratories using either flask samples, air tanks or pure CO_2 standards. Figure 8 summarizes these quality control insurance procedures.

Based on the first year of record of bleu and noir measurements, we end up with a mean reproducibility of 0.015 ‰ and 0.062‰ respectively for $\delta^{13}C$ and $\delta^{18}O$. Similar or better standard deviations are obtained within a single run sequence and deviation of the noir value with respect to the assigned true value is generally less than 0.05 for both isotopes.

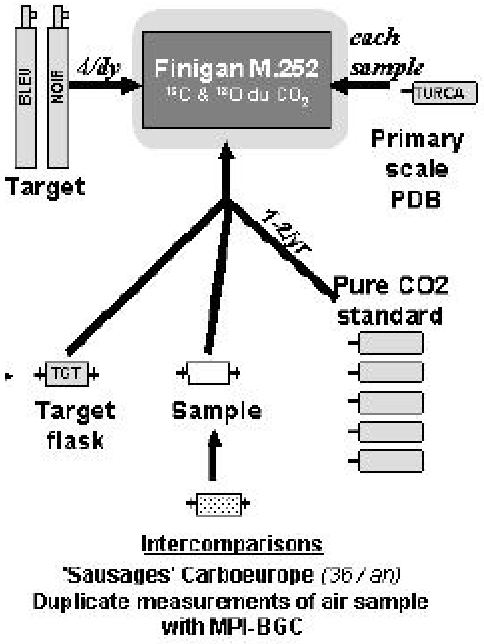

Figure 8: **Isotopic measurement quality control procedure followed at LSCE.**

5.6.4 Conclusion and Future Plans

During the last years we have extended and improved our flask analysis facility with a new GC and trapping box for our MS. This allows us to analyze about 2000 flasks per year. Two Loflo analyzers have been tested in our laboratory and are running now routinely at LSCE and at Amsterdam Island. We equipped two new sites Biscarosse, France (May-2005) and Hanle, India (August - 2005) with continuous CO_2 analyzers so called CARIBOUs developed at LSCE in collaboration with the CEA-DSM-DAPNIA. As part of a new project (Carbon network, funded by CEA) we will update the measurement instruments at Mace Head with a new CARIBOU and a GC (HP6890) at Puy de Dôme. In summer 2006 a GC (HP6890) and a CARIBOU we will installed at the new RAMCES “supersite” Orleans Tower. In addition to these activities regarding CO_2 we will initiate in 2006 hydrogen analyses at Saclay.

A main focus, however, will be the automation and real-time data transmission of our in-situ measurements. Moreover, the development of the LSCE database should be finished soon.

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5.7 CO_2 and CH_4 measurements at Cape Point, South Africa

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5.7.1 Introduction

Measurements of CO_2 and CH_4 have been made at Cape Point (CPT, 34 °S, 18 °E, at the southern tip of the Cape Peninsula) since 1993 and 1983, respectively. CO_2 measurements are related to the WMO X2002 scale through eight NOAA/ESRL-certified laboratory standards with mole fractions ranging from 353 to 396 ppm. For CH_4, eight laboratory standards (NOAA/CMDL 83 scale) are available at the site with mole fractions ranging from 1709 to 1879 ppb. Working gases are prepared at the laboratory by using an oil-free RIX compressor for dried ambient air, some suitably spiked or diluted to achieve a desired mole fraction. These working gases are then calibrated on a regular basis against our laboratory standards and possible CO_2 drift tracked. Filtering of data with respect to background concentrations is achieved by two different techniques, one being based on cut-off or threshold values, defined by moving percentiles, the other one by making use of the terrestrial tracer ^{222}Rn. The dominant clean-air sector at the site constitutes the southeastern to western quadrant. Figure 1 shows the angular distribution of ^{222}Rn and CO. They both clearly indicate the maritime baseline sector.

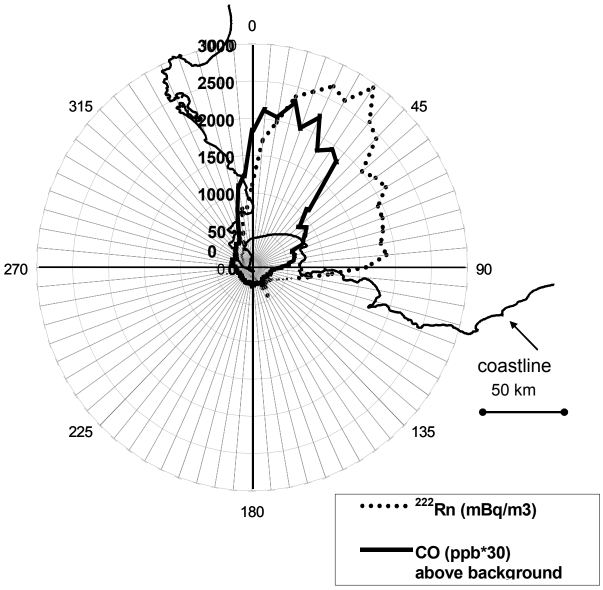

Figure 1: Clean-air sector at Cape Point as evidenced by the angular distribution of ^{222}Rn and CO. In addition, the coastline (with separate scale) is shown with the location of the station in the centre of the circle.

5.7.2 CO_2 Analytical System

The currently used URAS 4 NDIR analyser was installed at CPT in 1993. Ambient air is passed through a two-stage moisture trap (alcohol freezer maintained at -5°C and -45°C, respectively) and in addition through a magnesium perchlorate filter. This set-up effectively dries the ambient air to a dew point of about -70°C. Inter-comparisons of laboratory standards with working standards are performed twice monthly, whilst instrument calibrations using two working standards are made every six hours. Results from daily target gas analyses show that the monitoring system has a reproducibility of 0.01% or 0.04 ppm at a level of 369.77 ppm. Historically, the analyser's sensitivity remained fairly constant, changing from about 8.44 to 8.07 ppm per Volt over the past twelve years, possibly in response to an ageing IR source and/or detector.

Two of the NOAA/ESRL laboratory standards (in use since 1998 and re-analysed again in 2003) have shown good chemical stability over the years (variation: 0.04 and 0.08 ppm CO_2 respectively). These standards have been used as reference for all other cylinders. On the basis hereof, temporal decay of CO_2 mole fractions has been observed in most working standards (B30 Luxfer aluminium cylinders), but also in some of the laboratory standards. The rates of change are not consistent in sign and magnitude (range: -0.50 to 0.40 ppm yr^{-1}). It is speculated that the CO_2 decay in the working gases can most likely be attributed to some moisture within the cylinder mixture. In spite of the built-in water removal system of the RIX compressor in combination with two magnesium perchlorate cartridges (37 cm long; 3.3 cm ID) fitted in series, the likelihood of some moisture entering the cylinder cannot be excluded. The CO_2 mole fractions of the working standards are regularly monitored against a suite of our laboratory standards. Adjustments to the ambient data are then made according to the decay rate determined from these comparisons. The observed drift in some of the laboratory standards still needs clarification, however.

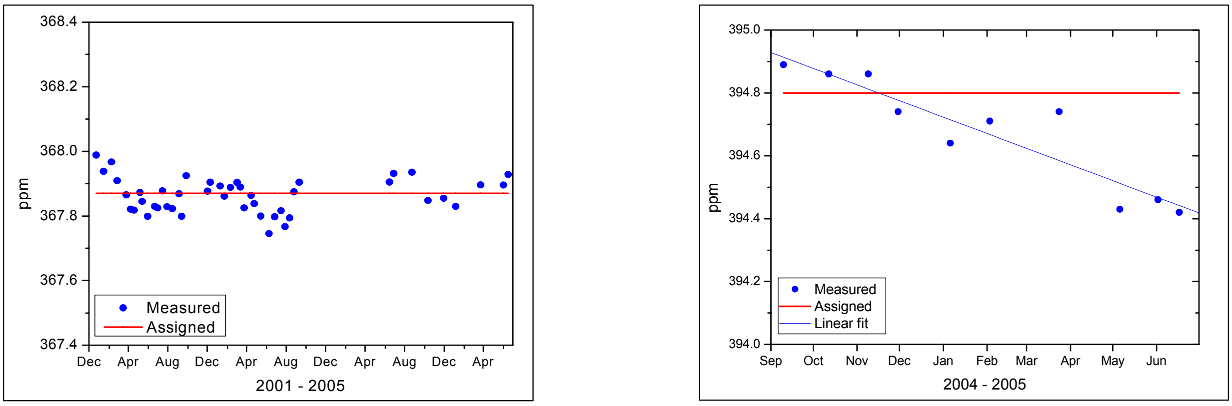

Figure 2: **Example of different drift behaviour for CO_2 standards. Working standard of good stability (left plot) and laboratory standard showing significant drift (right plot).**

5.7.3 CH_4 Analytical System

Methane measurements from 1983 till 2004 were made with a Carlo Erba (GC 6000) GC/FID system. In 2004 a new Varian gas chromatograph (CP3800) was installed. This has led to an improvement of reproducibility from 4.0 ppb to 2.7 ppb (1 s.d.) at 1730 ppb (N = 122).
The instrumental conditions used, are as follows:

FID temperature:	175 °C
Oven temperature:	80 °C
Sample loop:	9 mL
Column:	1 m x 1/4” o.d molecular sieve 13X (80/100 mesh)
Carrier gas	N_2 (5.0), 70 mL min^{-1}
FID air flow	255 mL min^{-1}
FID H_2 flow	32 mL min^{-1}

Analyses are run every 15 minutes, a 1-point calibration is performed once every hour, and a target gas is analysed once daily. Chromatograms are captured and processed via Azur software (DATALYS, France). The last audit by EMPA, Switzerland, was performed in 2002 and indicated that, on average, the Cape Point values were about 0.2 % above the WCC standards.

Figure 3 shows the CH_4 time series of monthly means for background conditions together with regression curve and trend. In addition the trend curve obtained with non-background data is plotted, which shows relatively stronger increase for the 1990s. In Figure 4 the average seasonal cycle of background CH_4 (2001 – 2004) is displayed in comparison with non-background observations. The data indicate strong inter-annual variability as well as similarities in the fine-structure for certain years. The yearly pairs 2002 and 2003 as well as 2001 and 2004 for instance show good agreement during the months of August and September.

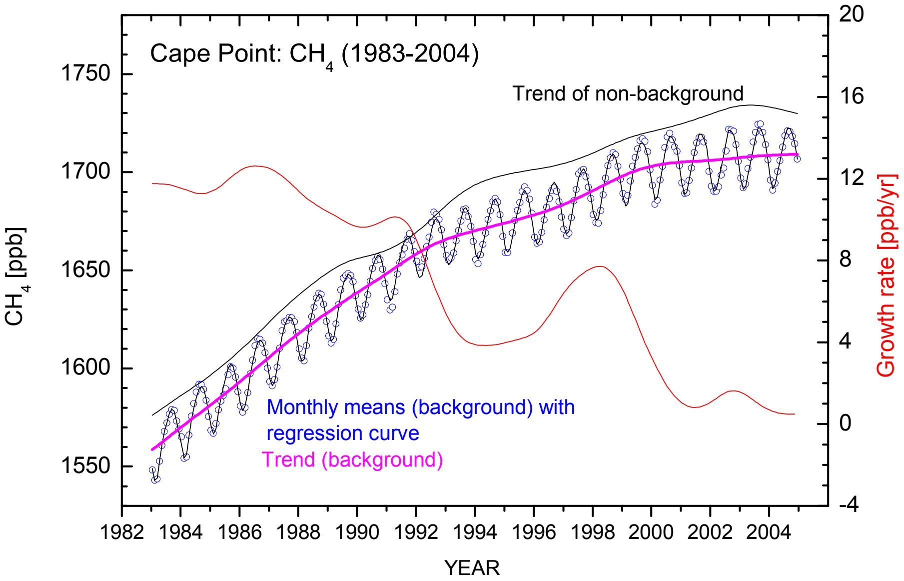

Figure 3: **CH_4 monthly means (background conditions) with regression and trend curve as well as growth rates. The black curve indicates the trend of the non-background data.**

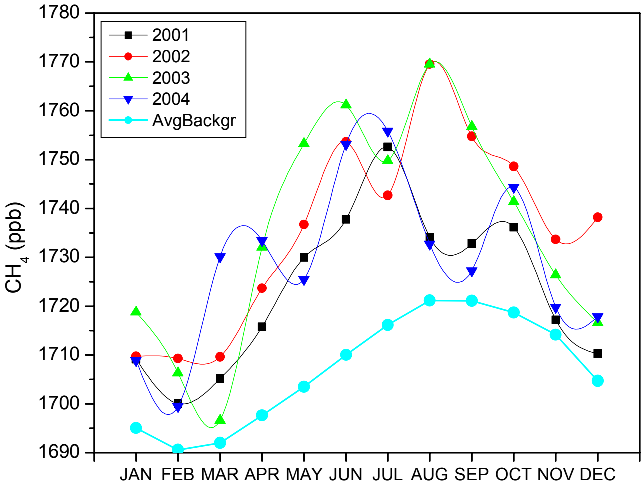

Figure 4: **CH_4 seasonal cycle: average background (2001 - 2004) in comparison with non-background observations showing strong inter-annual variability.**

5.7.4 Filtering of Data

The trace gas data collected at CPT comprise background levels, continental influences as well as short-term urban pollution. Baseline data for both CO_2 and CH_4 are obtained by removing continental and regional effects from the data set. Two different tools are employed as a selection criterion, a statistical filter as well as specific ^{222}Rn concentrations (e.g. < 100 mBq m^{-3}). For a detailed description of these filtering criteria, refer to Brunke *et al*. (2004). The statistical filter is based on 11- or 30-day moving percentiles (typically 5th and 95th), which can both be adjusted by an additional factor. In this way an upper and lower cut-off is created with the baseline data retained between these limits (Figures 5 and 6). A comparison with the ^{222}Rn selection techniques has shown that the statistical filter is sufficiently specific. An advantage of the ^{222}Rn criterion is that it is fully objective and not subject of decisions of the operator. Its disadvantage is the smaller data coverage. Furthermore, the statistical filter can be used for the entire time series, whilst the ^{222}Rn selection criterion is only available from 1999 onwards.

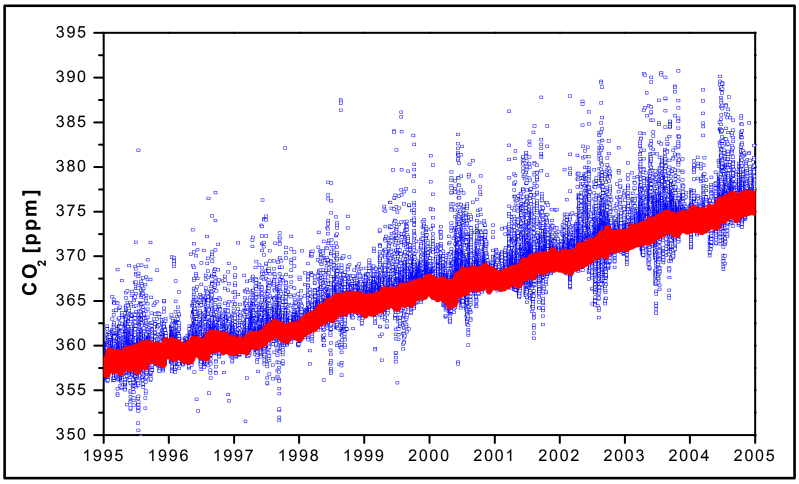

Figure 5: **CO_2 half-hourly means (1995 - 2004); all data (blue) and percentile filtered (red).**

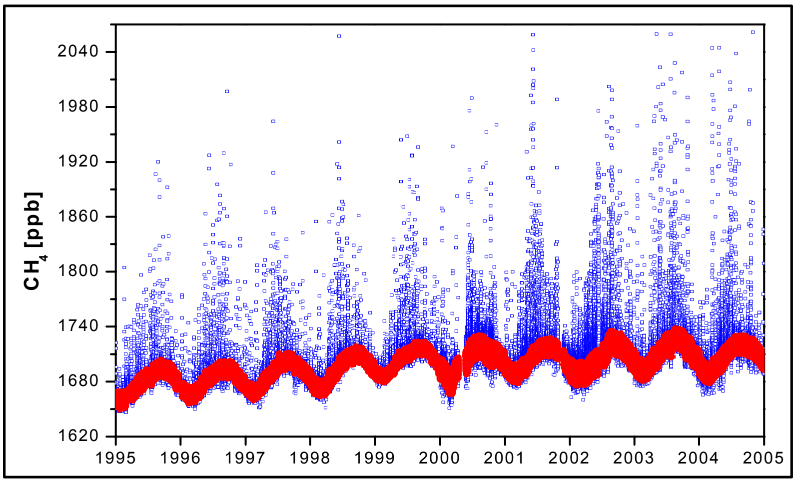

Figure 6: **CH_4 half-hourly means (1995 - 2004); all data (blue) and percentile filtered (red).**

5.7.5 Summary and Conclusions

More than 22 years of CH_4 and 12 years of CO_2 data are now available for Cape Point. The sensitivity of the URAS 4 instrument currently in use has remained fairly constant over the past 12 years. In order to improve the CO_2 data quality significantly, efforts will be made to upgrade the instrumentation with a LoFlo system. The CH_4 GC system has been replaced in 2004, resulting in some data quality improvement (currently 0.15% reproducibility). The use of a new column (HayeSep Q, 2 m x 1/8") did not yield better precision. With respect to CO_2, most of the working gases, but also a few laboratory standards have been found to be insufficiently stable. Additional moisture removing processes might have to be introduced to obtain drier working gases when compressing ambient air. The percentile filtering technique to extract baseline data from the all-data set has been verified by the ^{222}Rn selection technique and is being used for routine work. On a monthly basis, the overall shape of the CO_2 and CH_4 time series compares favourably with those of other southern hemispheric sites. With regard to minor deviations between sites, the CPT data quality obtained during recent years is estimated to be sufficient to provide useful information.

Acknowledgements

We would like to thank Danie van der Spuy for processing the raw data and Bhawoodien Parker for his IT support.

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5.8 Methane and Carbon Dioxide Continuous Measurements at Izana GAW Station (Spain)

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5.8.1 Introduction

Izaña Observatory is located at 2360 m above see level, on Tenerife (Canary Islands). Carbon dioxide and methane atmospheric mixing ratios have been continuously measured at Izaña since June 1984. During nighttime (20GMT-08GMT), in situ measurements are representative of free troposphere background conditions. This is due to the following facts: a) usually a strong subtropical temperature inversion layer is located at a lower altitude than Izana station; b) Izana station is located on the top of a crest, so during the night period downslope wind produces (by mass conservation) the arrival of free troposphere air to Izana.

In this paragraph, the content of this report is outlined. Measurement instruments and methods are summarized in section 2. In April 2005, we have started to rebuid (and improve) in Fortran 90 a numerical code for processing raw data to mixing ratios, and analysing them. A preliminary version of the new methane data processing scheme, which we have applied to the data period 2003-2004, is presented in section 3. Carbon dioxide (1984-2002) and methane (1984-2004) nighttime daily mean mixing ratio time series are analyzed (in section 4) using the usual decomposition in three terms: interannual trend, annual cycle, and residual, but using a method different from the previous literature. Finally, in section 5 we summarize near future plans for implementing and developing new techniques for data processing and analysis, and for implementing new greenhouse gas measurement programmes: N_2O and SF_6.

5.8.2 Methane and Carbon Dioxide Continuous Measurement Programmes

The general ambient air inlet, which provides ambient air for all instruments that analyze it, is a 8cm inner diameter (ID) stainless steel pipe and has a high flow rate. This inlet is situated on top of the building tower; the height above the ground has changed through the years: 13 m (1984-2000), 8 m (2000- May 2005) and 30 m (June 2005).

Methane mixing ratio is measured using a DANI 3800 gas chromatograph with an FID. The column is MoleSieve 13X 60/80 Mesh 1.20m x 1/4" O.D., 4 mm ID. The oven temperature is 55°C, whereas the FID temperature is 110°C. The carrier gas is synthetic air. Ambient air is cooled to -45 °C to partially remove water vapour content before flowing towards the sample loop (10 ml). There is an 8-port valve with two positions: load and inject. A few seconds before switching the 8-port valve from load to inject position, the flow through the sample loop is stopped to balance internal loop and ambient pressures (diffusion of ambient air into the sample loop is prevented by a 2 m outlet). Sample loop temperature is not regulated. A software integrator provides the area and height of the CH_4 peak in the chromatogram. Four samples are automatically measured every hour: at 00 and 30 minutes the sample is ambient air, at 15 and 45 minutes the sample is working gas. The working gas tank is calibrated every two weeks against the methane Izana primary standard (prepared by NOAA/ESRL). In December 2004, WCC-Empa carried out a system and performance audit for surface ozone, carbon monoxide and methane at Izana (Zellweger et al.,2005). For methane, the report concludes: “The results of the inter-comparisons between the five WCC-Empa travelling standards and the GC system of Izaña showed good agreement over the concentrations range of 1790 to 1880 ppb. The audit results at Izaña are good when compared to methane audits conducted by WCC-Empa at other GAW sites. The station instrument also showed reasonable repeatability. Due to the good results no technical recommendations are made by WCC-Empa.”

Carbon dioxide mixing ratio is measured with a SIEMENS Ultramat 3 NDIR analyzer. A cryocool trap is used to reduce the dew point of ambient air and standard gases to -65 °C. Three levels of standard gases are used (primary, secondary and working gases). Between calibrations, ambient air is analyzed continuously; mean value and standard deviation are recorded every 10 minutes. Daily 20GMT-08GMT carbon dioxide mean mixing ratio (in the WMO scale) for the period

1984-2002 is shown in Figure 1. Details about the measurement system and processing can be found in Ripodas et al. (2000), and Navascues and Rus, (1991).

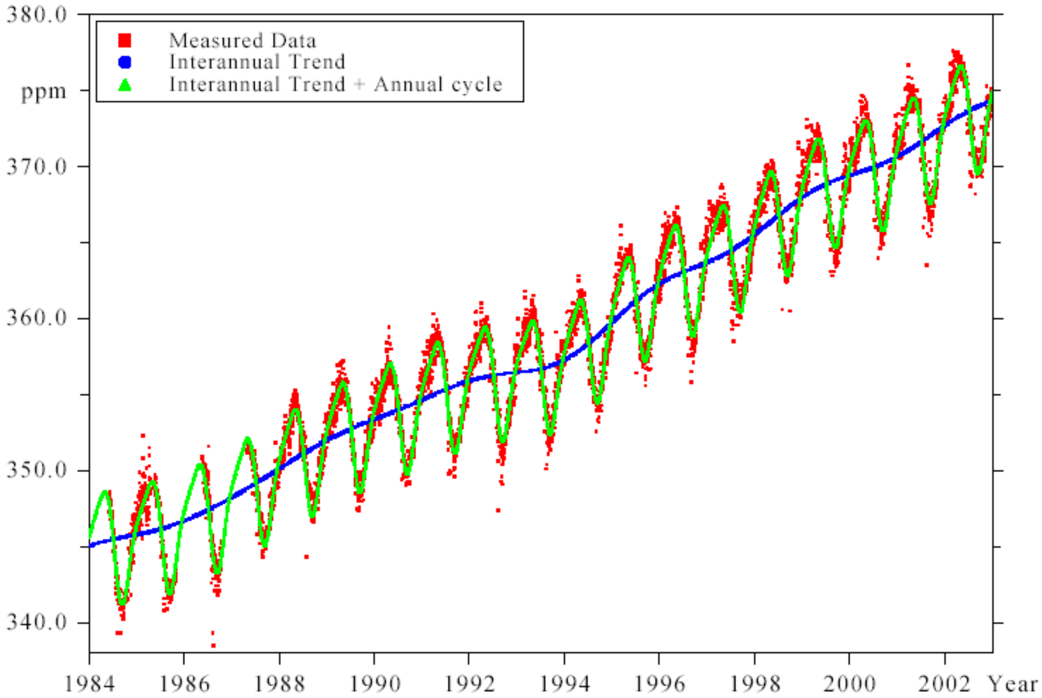

Figure 1: **Carbon Dioxide daily nighttime mean mixing ratio at Izana Observatory (INM).**

5.8.3 Processing Methane Raw Data To Mixing Ratios

In April 2005, we started to rebuid and improve, in Fortran 90, numerical code for processing methane raw data to mixing ratios. A preliminary version of the methane new data processing scheme, which we have applied to the data period 2003-2004, is presented here.

The response of the FID is assumed to be linear in methane mixing ratio (as it is usually stated in the literature). However, the response changes slowly with time due to variations in ambient conditions (pressure and temperature) and long term drift of the instrument. Peak area is used for data processing. We define the *response slope* (*RS*) of the instrument as the ratio: *(peak area/mixing ratio). RS* does not depend on mixing ratio, but does depend on time.

The data processing concerning the calibration of the working tank has not been changed yet. This tank is calibrated against the Izana methane primary standard every two weeks. The calibration sequence is as follows: every 5 minutes a gas is measured; the standard gas is measured first and then the working gas; this cycle is repeated 7 times, and the process is finished measuring the standard gas. So, for each calibration, there are 7 values for the mixing ratio of the working gas (the *RS* is obtained for the times in which the standard gas is measured, and it is assumed that *RS* changes linearly in time between adjacent standard gas measurements); mean value and standard deviation for the mixing ratio of the working tank are obtained. Typically, a working tank lasts 3.5 moths and is calibrated 8 times during its whole life. A unique value for the mixing ratio (the mean of the 8 calibrations) is used for the whole life of the working tank (usually no significant trend is observed in the mixing ratio of the working tank).

To detect and discard data obtained when the measurement instrument is not properly operating, we have implemented the following statistical procedure, which has been applied to the data period 2003-2004.

First, we consider the peak area time series (one value every 30 minutes) for the working gas. Dividing each value of these series by the corresponding working gas mixing ratio, we obtain the *RS* time series (*RS[t]*). For discarding outliers in the *RS* time series, the following steps are applied:

a) The time series $r(t) = RS(t) - \{RS(t)\}_{30.01d}$ is computed ($\{\ \}_{30.01d}$ indicates a 30.01 days running mean). Values *RS(t)* which have an associated $|r(t)|$ larger than $3.5\sqrt{\langle r^2(t)\rangle}$ are discarded ($\langle\ \rangle$ indicates series mean). $RS_a(t)$ denotes the *RS(t)* time series without those discarded values.

b) The time series $r(t) = RS_a(t) - \{RS_a(t)\}_{3.01d}$ is computed. Values $RS_a(t)$ which have an associated $|r(t)|$ larger than $3.5\sqrt{\langle r^2(t)\rangle}$ are discarded. $RS_b(t)$ denotes the $RS_a(t)$ time series without those discarded values.

c) The time series $r(t) = RS_b(t) - \{RS_b(t)\}_{0.26d}$ is computed. Values $RS_b(t)$ which have an associated $|r(t)|$ larger than $3\sqrt{\langle r^2(t)\rangle}$ are discarded. $RS_c(t)$ denotes the $RS_b(t)$ time series without those discarded values.

The 0.26-day running mean does not remove the *RS(t)* daily cycle, whereas the 30.01 and 3.01 days running means do. Because of this reason, we use a 3σ threshold for step c), and a 3.5σ threshold for steps a) and b). As an example, for the data period 2003-2004, 1.97% of the values in *RS(t)* have been discarded applying those three steps.

Second, we consider the peak area time series (one value every 30 minutes) for the ambient air: *A(t).* The time series $A_1(t)$ is built with the values *A(t)* for which values of $RS_c(t)$ from 15 minutes earlier and 15 minutes later are available. For the data period 2003-2004, 3.28% of the values in *A(t)* have been discarded applying this criterion. The time series *MR(t),* with the values of ambient methane mixing ratio, is computed using $MR(t) = A_1(t)/RS_d(t)$, where $RS_d(t)$ is the response slope in the times in which ambient air is measured. $RS_d(t)$ is obtained from $RS_c(t)$ by linear interpolation.

Third, for discarding outliers in the *MR(t)* time series, the steps a), b) and c) are applied to *MR(t)* . For the data period 2003-2004, 2.55% of the values in *MR(t)* have been discarded applying those three steps. Daily 20GMT-08GMT methane mean mixing ratio (in the CMDL83 scale) for the period 1984-2004 is shown in Figure 2.

5.8.4 Interannual Trend and Annual Cycle

Carbon dioxide (January 1th, 1984-December 31th, 2002) and methane (January 1th, 1984-December 31th, 2004) nighttime daily mean mixing ratio time series are analyzed using the usual decomposition in three terms: interannual trend, annual cycle, and residual, but using a method different from the previous literature. We carry out a least squares fit of the daily data to the function

$$f(t) = a_1 + a_2 t + \sum_{i=1}^{p} \left[b_i \cos(\omega_i t) + c_i \sin(\omega_i t)\right] + \sum_{j=1}^{4} \left[d_j \cos(k_j t) + e_j \sin(k_j t)\right]$$

where: t is the time in days (t=1 for January 1th, 1984); a_1, a_2, b_i and c_i are the parameters of the interannual trend to be determined; $p = 7$ for the methane analysis and $p = 6$ for the carbon dioxide analysis; d_j and e_j are the parameters of the annual cycle (which is assumed constant) to be determined; $\omega_i = 2\pi i/N$ where N equals the number of days in the considered period

($N = 7671$ for the methane analysis, $N = 6940$ for the carbon dioxide analysis); $k_j = 2\pi j / T$ with $T = 365.25$ days. The interannual trend in *f(t)* has two contributions: a linear term in *t,* and the discrete Fourier modes corresponding to the lowest *p* Fourier frequencies for an *N* points domain (the linear trend is introduced to allow the periodic function, with period *N* days, described by the Fourier modes to be continuous). We define the cut off frequency (linear) as $f_c = p/N$ ($f_c = 0.333$ year^{-1} for the methane analysis and $f_c = 0.316$ year^{-1} for the carbon dioxide analysis). The cut off frequency is the largest frequency in the considered interannual trend. The annual cycle term in *f(t)* is composed by the discrete Fourier modes of one year period and its first three harmonics.

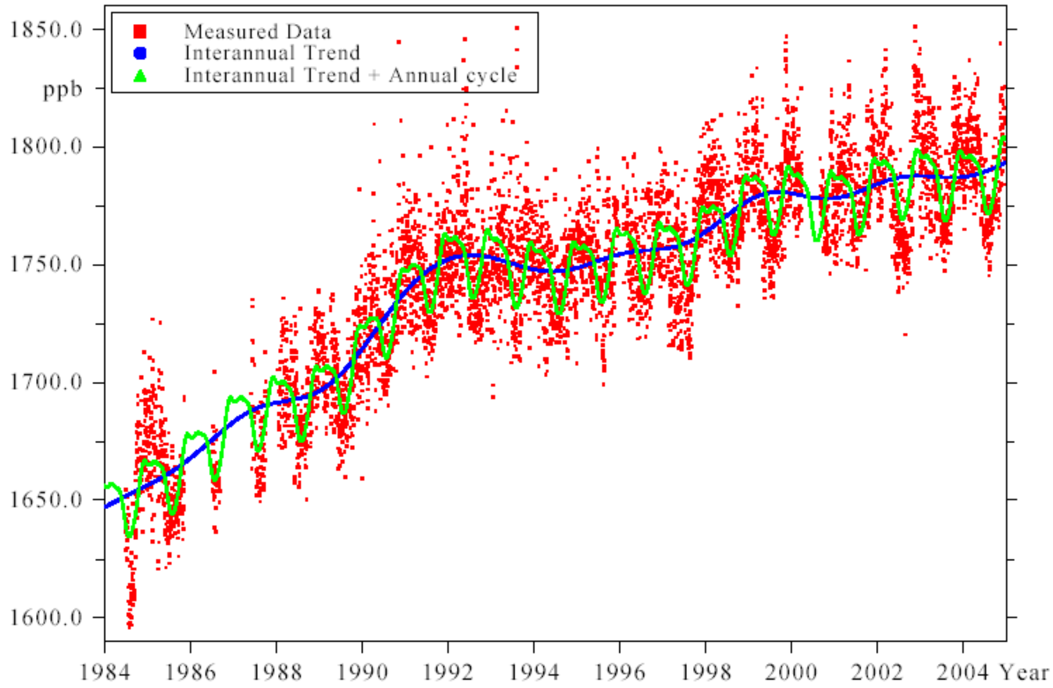

Figure 2: **Methane daily nighttime mean mixing ratio at Izana Observatory (INM).**

Other authors have obtained the Fourier transform directly (e.g. Thoning et al., 1989) or after applying a second order polynomial and annual cycle fit (e.g. Dlugokencky et al., 1994), and have applied two low-pass filters: one to obtain the interannual trend, and the other one to obtain a smoothed representation of the data. However, Fourier transform requires that the data be equally spaced in time and without gaps. So, data gaps must be filled by interpolation (e.g. Thoning et al., 1989, use linear interpolation). Interpolation introduces information that was not present in the original data. Our method to obtain interannual trend and constant annual cycle does not require interpolation.

Figures 1 and 2 show the interannual trend and the interannual trend+annual cycle for carbon dioxide and methane, respectively. Figure 3 shows the annual cycle for methane and carbon dioxide. For carbon dioxide, the standard deviation of the residuals is 0.84 ppm, the interannual mean growth rate for the period 1984-2002 is 1.54 ppm/year; the peak-to-peak annual cycle amplitude is 7.7 ppm; the annual cycle has its maximum at the beginning of May and its minimum at middle September. For methane, the standard deviation of the residuals is 17.4 ppb, the interannual mean growth rates for the periods: 1984-1991 is 13.1 ppb/year, 1992-1997 is 1.9 ppb/year, 1998 is 13.4 ppb/year, 1999-2004 is 2.7 ppb/year; the peak-to-peak annual cycle amplitude is 29.5 ppb; the annual cycle has its maximum at the beginning of December (with a plateau in winter) and its minimum at the beginning of August.

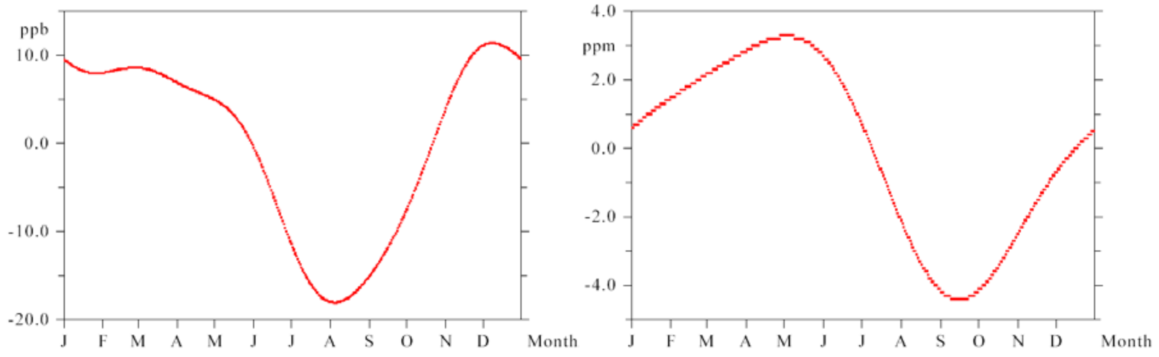

Figure 3: **Mean annual cycle for methane and carbon dioxide at Izana Observatory (INM).**

5.8.5 Near Future Plans

A Varian 3800 GC has been installed with two detectors: a FID to measure CH_4, and an ECD to measure N_2O and SF_6. In a few months, after optimizing the configuration of this instrument, routine atmospheric measurements will be started. A LI-COR 6252 NDIR analyzer will be installed to measure CO_2. So, CH_4 and CO_2 measurements will be duplicated. We are going to continue implementing and developing new techniques for CH_4, CO_2, N_2O and SF_6 data processing and analysis.

We acknowledge Dr E. Cuevas, for his comments, and the meteorological observer team of Izana: C. Hernandez, D. Martin and R. Juega.

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151. Report of the First CAS Working Group on Environmental Pollution and Atmospheric Chemistry (Geneva, Switzerland, 18-19 March 2003) (WMO TD No. 1181).

152. Current Activities of the Global Atmosphere Watch Programme (as presented at the 14th World Meteorological Congress, May 2003). (WMO TD No. 1168).

153. WMO/GAW Aerosol Measurement Procedures: Guidelines and Recommendations. (WMO TD No. 1178).

154. WMO/IMEP-15 Trace Elements in Water Laboratory Intercomparison. (WMO TD No. 1195).

155. 1st International Expert Meeting on Sources and Measurements of Natural Radionuclides Applied to Climate and Air Quality Studies (Gif sur Yvette, France, 3-5 June 2003) (WMO TD No. 1201).

156. Addendum for the Period 2005-2007 to the Strategy for the Implementation of the Global Atmosphere Watch Programme (2001-2007), GAW Report No. 142 (WMO TD No. 1209).

157. JOSIE-1998 Performance of EEC Ozone Sondes of SPC-6A and ENSCI-Z Type (Prepared by Herman G.J. Smit and Wolfgang Straeter) (WMO TD No. 1218).

158. JOSIE-2000 Jülich Ozone Sonde Intercomparison Experiment 2000. The 2000 WMO international intercomparison of operating procedures for ECC-ozone sondes at the environmental simulation facility at Jülich (Prepared by Herman G.J. Smit and Wolfgang Straeter) (WMO TD No. 1225).

159. IGOS-IGACO Report - September 2004 (WMO TD No. 1235)

160. Manual for the GAW Precipitation Chemistry Programme (Guidelines, Data Quality Objectives and Standard Operating Procedures) (WMO TD No. 1251).

161 12th WMO/IAEA Meeting of Experts on Carbon Dioxide Concentration and Related Tracers Measurement Techniques (Toronto, Canada, 15-18 September 2003).

162. WMO/GAW Experts Workshop on a Global Surface-Based Network for Long Term Observations of Column Aerosol Optical Properties, Davos, Switzerland, 8-10 March 2004 (edited by U. Baltensperger, L. Barrie and C. Wehrli) (WMO TD No. 1287).

163. World Meteorological Organization Activities in Support of the Vienna Convention on Protection of the Ozone Layer (WMO No. 974).

164. Instruments to Measure Solar Ultraviolet Radiation: Part 2: Broadband Instruments Measuring Erythemally Weighted Solar Irradiance (WMO TD No. 1289).

165. Report of the CAS Working Group on Environmental Pollution and Atmospheric Chemistry and the GAW 2005 Workshop, 14-18 March 2005, Geneva, Switzerland (WMO TD No. 1302).

166. Joint WMO-GAW/ACCENT Workshop on The Global Tropospheric Carbon Monoxide Observations System, Quality Assurance and Applications (EMPA, Dübendorf, Switzerland, 24 – 26 October 2005) (edited by J. Klausen) (WMO TD No. 1335).

167. The German Contribution to the WMO Global Atmosphere Watch Programme upon the 225th Anniversary of GAW Hohenpeissenberg Observatory (edited by L.A. Barrie, W. Fricke and R. Schleyer (WMO TD No. 1336).

168. The 13th WMO/IAEA Meeting of Experts on Carbon Dioxide Concentration and Related Tracers Measurement Techniques (Boulder, Colorado, USA, 19-22 September 2005) (WMO TD No. 1359).

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